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Chapter 2

Thermodynamics

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  An excellent thermodynamics text appropriate for upper division undergraduates. Contains many illustrative practical applications.
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  Lively modern text with excellent choice of topics and good historical content. More focus on chemical and materials applications than in Callen.
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2.2 What is Thermodynamics?

Thermodynamics is the study of relations among the *state variables* describing a thermodynamic system, and of transformations of heat into work and *vice versa*.

2.2.1 Thermodynamic systems and state variables

Thermodynamic systems contain large numbers of constituent particles, and are described by a set of *state variables* which describe the system's properties in an average sense. State variables are classified as being either *extensive* or *intensive*.

Extensive variables, such as volume V, particle number N, total internal energy E, magnetization M, *etc.*, scale linearly with the system size, *i.e.* as the first power of the system volume. If we take two identical thermodynamic systems, place them next to each other, and remove any barriers between them, then all the extensive variables will double in size.

Intensive variables, such as the pressure p, the temperature T, the chemical potential μ, the electric field $\boldsymbol{E}$, *etc.*, are independent of system size, scaling as the zeroth power of the volume. They are the same throughout the system, if that system is in an appropriate state of *equilibrium*. The ratio of any two extensive variables is an intensive variable. For example, we write $n = N/V$ for the number density, which scales as V^0. Intensive variables may also be *inhomogeneous*. For example, $n(\boldsymbol{r})$ is the number density at position $\boldsymbol{r}$, and is defined as the limit of $\Delta N/\Delta V$ of the number of particles ΔN inside a volume ΔV which contains the point $\boldsymbol{r}$, in the limit $V \gg \Delta V \gg V/N$.

Heat and work are *not* state variables. That is to say, we cannot meaningfully speak of the heat or work of a thermodynamic system the way we can speak of its energy or pressure. Rather, what is meaningful is the heat Q added to a system, say that supplied to a kettle of water on a hot stove, or the work W done by a system, say by an expanding gas which pushes on a piston head. Both Q and W have dimensions of energy, and conservation of energy then entails that the internal energy change ΔE of a thermodynamic system is given by $\Delta E = Q - W$, which is the First Law of Thermodynamics. As a crude analogy, think of your bank account. You can deposit or withdraw funds in the form of checks or cash, which might be likened to thermodynamic heat and work, each having the units of US dollars. But the bank just keeps track of the total dollar value of your account, which is analogous to the total energy. You cannot say that your account consists of so much in checks, so much in bills, or, at a more refined level, so much in singles, fives, tens, twenties, *etc.*

Classically, the full motion of a system of N point particles requires $6N$ variables to fully describe it ($3N$ positions and $3N$ velocities or momenta, in three space dimensions)[1]. Since the constituents are very small, N is typically very large. A typical solid or liquid, for example, has a mass density on the order of $\varrho \sim 1\,\mathrm{g/cm^3}$; for gases, $\varrho \sim 10^{-3}\,\mathrm{g/cm^3}$. The constituent atoms have masses of 10^0 to 10^2 grams per mole, where one mole of X contains $N_{\rm A}$ of X, and $N_{\rm A} = 6.022140765 \times 10^{23}$ is Avogadro's number[2]. Thus, for solids and liquids we roughly expect number densities n of $10^{-2} - 10^0\,\mathrm{mol/cm^3}$ for

[1] For a system of N molecules which can freely rotate, we must then specify $3N$ additional orientational variables – the Euler angles – and their $3N$ conjugate momenta. The dimension of phase space is then $12N$.

[2] Hence, 1 guacamole = 6.0221415×10^{23} guacas.

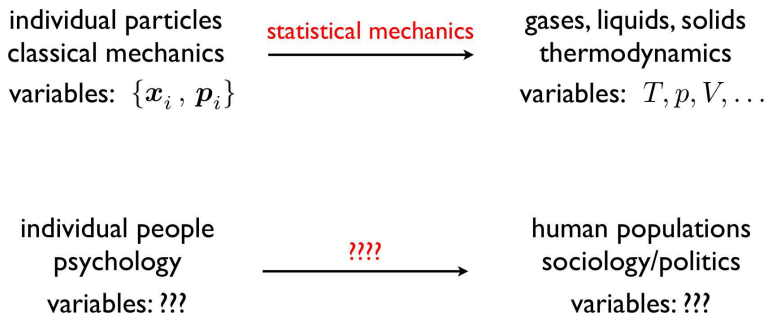


Figure 2.1: From microscale to macroscale : physical *versus* social sciences.

solids and liquids, and $10^{-5} - 10^{-3}\,\mathrm{mol/cm^3}$ for gases. Clearly we are dealing with fantastically large numbers of constituent particles in a typical thermodynamic system. The underlying theoretical basis for thermodynamics, where we use a small number of state variables to describe a system, is provided by the microscopic theory of statistical mechanics, which we shall study in the weeks ahead.

Intensive quantities such as p, T, and n ultimately involve averages over both space and time. Consider for example the case of a gas enclosed in a container. We can measure the pressure (relative to atmospheric pressure) by attaching a spring to a moveable wall, as shown in fig. 2.2. From the displacement of the spring and the value of its spring constant k we determine the force F. This force is due to the difference in pressures, so $p = p_0 + F/A$. Microscopically, the gas consists of constituent atoms or molecules, which are constantly undergoing collisions with each other and with the walls of the container. When a particle bounces off a wall, it imparts an impulse $2\hat{\boldsymbol{n}}(\hat{\boldsymbol{n}} \cdot \boldsymbol{p})$, where $\boldsymbol{p}$ is the particle's momentum and $\hat{\boldsymbol{n}}$ is the unit vector normal to the wall. (Only particles with $\boldsymbol{p} \cdot \hat{\boldsymbol{n}} > 0$ will hit the wall.) Multiply this by the number of particles colliding with the wall per unit time, and one finds the net force on the wall; dividing by the area gives the pressure p. Within the gas, each particle travels for a distance ℓ, called the *mean free path*, before it undergoes a collision. We can write $\ell = \bar{v}\tau$, where $\bar{v}$ is the average particle speed and τ is the *mean free time*. When we study the kinetic theory of gases, we will derive formulas for ℓ and $\bar{v}$ (and hence τ). For now it is helpful to quote some numbers to get an idea of the relevant distance and time scales. For O_2 gas at standard temperature and pressure ($T = 0^\circ$ C, $p = 1$ atm), the mean free path is $\ell \approx 1.1 \times 10^{-5}$ cm, the average speed is $\bar{v} \approx 425\,\mathrm{m/s}$, and the mean free time is $\tau \approx 2.6 \times 10^{-10}$ s. Thus, particles in the gas undergo collisions at a rate $\tau^{-1} \approx 4.0 \times 10^9\,\mathrm{s^{-1}}$. A measuring device, such as our spring, or a thermometer, effectively performs time and space averages. If there are N_c collisions with a particular patch of wall during some time interval on which our measurement device responds, then the root mean square relative fluctuations in the local pressure will be on the order of $N_c^{-1/2}$ times the average. Since N_c is a very large number, the fluctuations are negligible.

If the system is in *steady state*, the state variables do not change with time. If furthermore there are no macroscopic currents of energy or particle number flowing through the system, the system is said to be in *equilibrium*. A continuous succession of equilibrium states is known as a *thermodynamic path*, which can be represented as a smooth curve in a multidimensional space whose axes are labeled by state variables. A thermodynamic *process* is any change or succession of changes which results in a change of the state variables. In a *cyclic* process, the initial and final states are the same. In a *quasistatic* process, the system passes through a continuous succession of equilibria. A *reversible* process is one where the external conditions and the thermodynamic path of the system can be reversed; it is both quasi-static

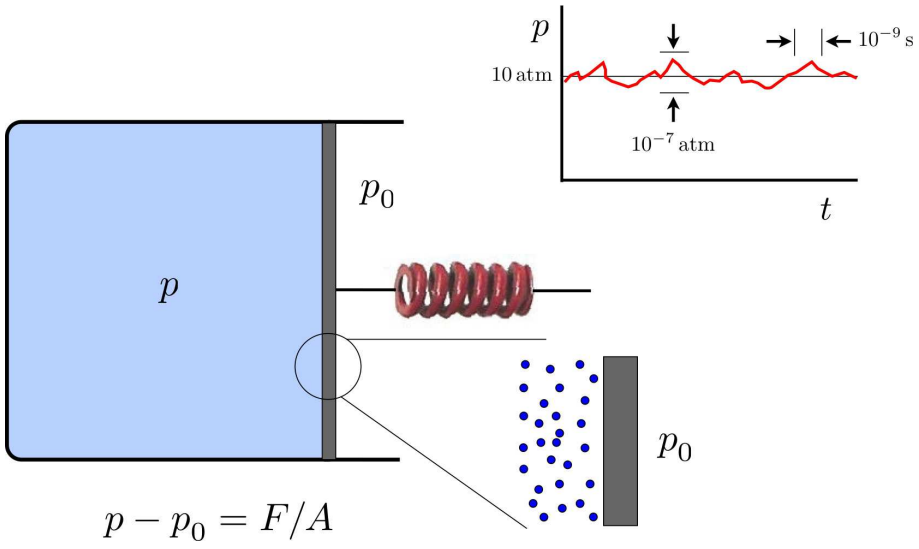


Figure 2.2: The pressure p of a gas is due to an average over space and time of the impulses due to the constituent particles.

and non-dissipative (*i.e.* no friction). The slow expansion of a gas against a piston head, whose counterforce is always infinitesimally less than the force pA exerted by the gas, is reversible. To reverse this process, we simply add infinitesimally more force to pA and the gas compresses. An example of a quasistatic process which is not reversible: slowly dragging a block across the floor, or the slow leak of air from a tire. Irreversible processes, as a rule, are dissipative. Oftentimes we will concern ourselves with infinitesimal amounts of heat and work, and how these are related to infinitesimal changes in state variables. Expressed in terms of differentials, there are several special processes we will discuss:

$$\begin{aligned} \textit{reversible: } đQ &= T\,dS & \qquad \textit{isothermal: } dT &= 0 \\ \textit{spontaneous: } đQ &< T\,dS & \qquad \textit{isochoric: } dV &= 0 \\ \textit{adiabatic: } đQ &= 0 & \qquad \textit{isobaric: } dp &= 0 \quad . \end{aligned}$$

If ϕ is a state variable or a function of state variables, its infinitesimal change is expressed as $d\phi$, which is an *exact differential*. If ϕ is not a state variable, then its differential is in general *inexact*, and we express its infinitesimal change as $đ\phi$. We shall discuss the entropy S and its relation to irreversibility in §2.6.

2.2.2 Mathematical interlude : exact and inexact differentials

The differential

$$dF = \sum_{i=1}^{k} A_i\,dx_i \tag{2.1}$$

is called *exact* if there is a smooth function[3] $F(x_1, \ldots, x_k)$ whose differential gives the right hand side of eqn. 2.1. On a simply connected open domain, a differential with continuously differentiable coefficients

[3]Smoothness means that all partial derivatives exist and are continuous. In fact, this condition is needlessly stringent for our purposes. For exactness we only require that all the second partial derivatives exist and are

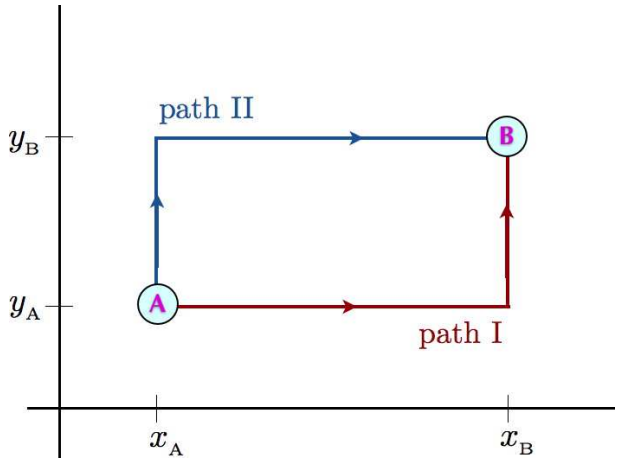


Figure 2.3: Two distinct paths with identical endpoints.

A_i is exact if and only if its cross derivatives agree, *viz.*

$$A_i = \frac{\partial F}{\partial x_i} \qquad \Longleftrightarrow \qquad \frac{\partial A_i}{\partial x_j} = \frac{\partial A_j}{\partial x_i} = \frac{\partial^2 F}{\partial x_i \partial x_j} \quad \forall\, i,j \tag{2.2}$$

for some single-valued function F. For exact differentials, the integral between fixed endpoints is path-independent:

$$\int_{\rm A}^{\rm B} dF = F(x_1^{\rm B},\ldots,x_k^{\rm B}) - F(x_1^{\rm A},\ldots,x_k^{\rm A}) \quad , \tag{2.3}$$

from which it follows that the integral of dF around any closed path must vanish: $\oint dF = 0$.

When the cross derivatives are not identical, *i.e.* when $\partial A_i/\partial x_j \neq \partial A_j/\partial x_i$, the differential is *inexact*. In this case, the integral of dF is path dependent, and does not depend solely on the endpoints.

As an example, consider the differential $dF = K_1\, y\, dx + K_2\, x\, dy$. Let's evaluate the integral of dF along each of the two paths in fig. 2.3:

$$F^{(\rm I)} = \int\limits_{\mathcal{C}_{\rm I}} dF = K_1 \int\limits_{x_{\rm A}}^{x_{\rm B}} dx\; y_{\rm A} + K_2 \int\limits_{y_{\rm A}}^{y_{\rm B}} dy\; x_{\rm B} = K_1\, y_{\rm A}\,(x_{\rm B} - x_{\rm A}) + K_2\, x_{\rm B}\,(y_{\rm B} - y_{\rm A}) \tag{2.4}$$

$$F^{(\rm II)} = \int\limits_{\mathcal{C}_{\rm II}} dF = K_1 \int\limits_{x_{\rm A}}^{x_{\rm B}} dx\; y_{\rm B} + K_2 \int\limits_{y_{\rm A}}^{y_{\rm B}} dy\; x_{\rm A} = K_1\, y_{\rm B}\,(x_{\rm B} - x_{\rm A}) + K_2\, x_{\rm A}\,(y_{\rm B} - y_{\rm A}) \quad , \tag{2.5}$$

continuous, which entails eqn. 2.2. The domain matters for global exactness. For example, the differential $(x\,dy - y\,dx)/(x^2+y^2)$ has equal cross derivatives on the punctured plane, but its integral around a counterclockwise circle enclosing the origin is 2π, so it is not exact there. Locally it is the differential $d\theta$ of an angular coordinate θ, but no single-valued angular coordinate exists on the entire punctured plane.

where $\mathcal{C}_{\rm I,II}$ are, respectively, paths I and II. Note that in general $F^{\rm (I)} \neq F^{\rm (II)}$. Thus, if we start at point A, the value of F at point B will depend on the path taken, since the change $\Delta F = \int_{\rm A}^{\rm B} dF$ is path-dependent. The difference in ΔF associated with each of the two paths is

$$F^{\rm (I)} - F^{\rm (II)} = \oint_{\mathcal{C}} dF = (K_2 - K_1)\,(x_{\rm B} - x_{\rm A})\,(y_{\rm B} - y_{\rm A}) \quad , \tag{2.6}$$

where $\mathcal{C} = \mathcal{C}_{\rm II}^{-1} \circ \mathcal{C}_{\rm I}$ is the closed path formed by appending the reverse of path II (*i.e.* $C_{\rm II}^{-1}$) to path I. Thus, we see that if $K_1 = K_2$, the work is the same for the two paths. In fact, if $K_1 = K_2$, the work would be path-independent, and would depend only on the endpoints. This is true for *any* path, and not just piecewise linear paths of the type depicted in fig. 2.3. Thus, if $K_1 = K_2$, we are justified in using the notation dF for the differential. Explicitly, we then have $F = K_1 xy$. However, if $K_1 \neq K_2$, the differential is inexact, and we will henceforth write $đF$ in such cases.

2.2.3 Equations of state

How many state variables are necessary to fully specify the equilibrium state of a thermodynamic system? For a single component system, such as water which is composed of one molecular species, the answer is three. These can be taken to be T, p, and V. One always must specify at least one extensive variable, else we cannot determine the overall size of the system. We shall discuss this question in detail in §2.3.1 and §2.11.5 below. For a multicomponent system with c different species, we must specify $\mathsf{c}+2$ state variables, which may be $\{T, p, N_1, \ldots, N_{\mathsf{c}}\}$, where N_a is the number of particles of species a. Another possibility is the set $\{T, p, V, x_1, \ldots, x_{\mathsf{c}-1}\}$, where the *concentration* of species a is $x_a = N_a/N$. Here, $N = \sum_{a=1}^{\mathsf{c}} N_a$ is the total number of particles. Note that $\sum_{a=1}^{\mathsf{c}} x_a = 1$.

It then follows that if we specify more than $\mathsf{c}+2$ state variables, there must exist a relation among them. Such relations are known as *equations of state*. The most famous example is the ideal gas law,

$$pV = Nk_{\rm B}T \quad , \tag{2.7}$$

relating the four state variables T, p, V, and N. Here $k_{\rm B} = 1.380649 \times 10^{-16}\,\mathrm{erg/K}$ is Boltzmann's constant. Another example is the van der Waals equation,

$$\left(p + \frac{\bar{a}N^2}{V^2}\right)(V - \bar{b}N) = Nk_{\rm B}T \quad , \tag{2.8}$$

where $\bar{a}$ and $\bar{b}$ are constants which depend on the molecule which forms the gas. For a third example, consider a paramagnet, where

$$\frac{M}{V} = \frac{CH}{T} \quad , \tag{2.9}$$

where M is the magnetization, H the magnetic field, and C the Curie constant.

Any quantity which, in equilibrium, depends only on the state variables is called a *state function*. For example, the total internal energy E of a thermodynamic system is a state function, and we may write $E = E(T, p, V)$. State functions can also serve as state variables, although the most natural state variables are those which can be directly measured.

2.2.4 Heat

Once thought to be a type of fluid, heat is now understood in terms of the kinetic theory of gases, liquids, and solids as a form of energy stored in the disordered motion of constituent particles. The units of heat are therefore units of energy, and it is appropriate to speak of *heat energy*, which we shall simply abbreviate as *heat*:[4]

$$1\,\mathrm{J} = 10^7\,\mathrm{erg} = 6.242\times10^{18}\,\mathrm{eV} = 2.390\times10^{-4}\,\mathrm{kcal} = 9.478\times10^{-4}\,\mathrm{BTU} \quad . \tag{2.10}$$

We will use the symbol Q to denote the amount of heat energy absorbed by a system during some given thermodynamic process, and $đQ$ to denote a differential amount of heat energy. The symbol $đ$ indicates an inexact differential (see §2.2.2). This means that heat is not a state function: there is no 'heat function' $Q(T,p,V)$.

2.2.5 Work

In general we will write the differential element of work $đW$ done *by* the system as

$$đW = \sum_i F_i\,dX_i \quad , \tag{2.11}$$

where F_i is a *generalized force* and dX_i a *generalized displacement*[5]. The generalized forces and displacements are themselves state variables, and by convention we will take the generalized forces to be *intensive* and the generalized displacements to be *extensive*. As an example, in a simple one-component system, we have $đW = p\,dV$. More generally, we write

$$đW = \overbrace{\big(p\,dV - \boldsymbol{H}\cdot d\boldsymbol{M} - \boldsymbol{E}\cdot d\boldsymbol{P} - \sigma\,dA + \ldots\big)}^{-\sum_j y_j\,dX_j} - \overbrace{\big(\mu_1\,dN_1 + \mu_2\,dN_2 + \ldots\big)}^{\sum_a \mu_a\,dN_a} \tag{2.12}$$

Here we distinguish between two types of work. The first involves changes in quantities such as volume, magnetization, electric polarization, area, *etc.* The conjugate forces y_i applied *to* the system are then $-p$, the magnetic field $\boldsymbol{H}$, the electric field $\boldsymbol{E}$, the surface tension σ, respectively. The second type of work involves changes in the number of constituents of a given species. For example, energy is required in order to dissociate two hydrogen atoms in an H_2 molecule. The effect of such a process is $dN_{\mathrm{H}_2} = -1$ and $dN_{\mathrm{H}} = +2$. Thus, $đW = -\boldsymbol{y}\cdot d\boldsymbol{X} - \boldsymbol{\mu}\cdot d\boldsymbol{N}$, with $\boldsymbol{X} = \{X_1,\ldots,X_{\mathsf{d}}\}$ and $N = \{N_1,\ldots,N_{\mathsf{c}}\}$. In this general setting there are d generalized displacements and c component species. When $\mathsf{d} = 1$, the volume is the only displacement.

As with heat, $đW$ is an inexact differential, and work W is not a state variable, since it is path-dependent. There is no 'work function' $W(T,p,V)$.

[4] One calorie (cal) is the amount of heat needed to raise $1\,\mathrm{g}$ of $\mathrm{H_2O}$ from $T_0 = 14.5^\circ\,\mathrm{C}$ to $T_1 = 15.5^\circ\,\mathrm{C}$ at a pressure of $p_0 = 1\,\mathrm{atm}$. One British Thermal Unit (BTU) is the amount of heat needed to raise $1\,\mathrm{lb}$. of $\mathrm{H_2O}$ from $T_0 = 63^\circ\,\mathrm{F}$ to $T_1 = 64^\circ\,\mathrm{F}$ at a pressure of $p_0 = 1\,\mathrm{atm}$.

[5] We use the symbol $đ$ in the differential $đW$ to indicate that this is not an exact differential. More on this in section 2.2.2.

2.2.6 Pressure and temperature

The units of pressure (p) are force per unit area. The SI unit is the Pascal (Pa): $1\,\mathrm{Pa} = 1\,\mathrm{N/m^2} = 1\,\mathrm{kg/m\,s^2}$. Other units of pressure we will encounter:

$$1\,\mathrm{bar} \equiv 10^5\,\mathrm{Pa} \quad , \quad 1\,\mathrm{atm} \equiv 1.01325 \times 10^5\,\mathrm{Pa} \quad , \quad 1\,\mathrm{torr} \equiv 133.3\,\mathrm{Pa} \quad .$$

Temperature (T) has a very precise definition from the point of view of statistical mechanics, as we shall see. Many physical properties depend on the temperature – such properties are called *thermometric properties*. For example, the resistivity of a metal $\rho(T,p)$ or the number density of a gas $n(T,p)$ are both thermometric properties, and can be used to define a temperature scale. Consider the device known as the 'constant volume gas thermometer' depicted in fig. 2.4, in which the volume or pressure of a gas may be used to measure temperature. The gas is assumed to be in equilibrium at some pressure p, volume V, and temperature T. An incompressible fluid of density ϱ is used to measure the pressure difference $\Delta p = p - p_0$, where p_0 is the ambient pressure at the top of the reservoir:

$$p - p_0 = \varrho g(h_2 - h_1) \quad , \tag{2.13}$$

where g is the acceleration due to gravity. The height h_1 of the left column of fluid in the U-tube provides a measure of the change in the volume of the gas:

$$V(h_1) = V(0) - Ah_1 \quad , \tag{2.14}$$

where A is the (assumed constant) cross-sectional area of the left arm of the U-tube. The device can operate in two modes:

- Constant pressure mode : The height of the reservoir is adjusted so that the height difference $h_2 - h_1$ is held constant. This fixes the pressure p of the gas. The gas volume still varies with temperature T, and we can define
$$\frac{T}{T_{\rm ref}} = \frac{V}{V_{\rm ref}} \quad , \tag{2.15}$$
where $T_{\rm ref}$ and $V_{\rm ref}$ are the reference temperature and volume, respectively.
- Constant volume mode : The height of the reservoir is adjusted so that $h_1 = 0$, hence the volume of the gas is held fixed, and the pressure varies with temperature. We then define
$$\frac{T}{T_{\rm ref}} = \frac{p}{p_{\rm ref}} \quad , \tag{2.16}$$
where $T_{\rm ref}$ and $p_{\rm ref}$ are the reference temperature and pressure, respectively.

What should we use for a reference? One might think that a pot of boiling water will do, but anyone who has gone camping in the mountains knows that water boils at lower temperatures at high altitude (lower pressure). This phenomenon is reflected in the *phase diagram* for H_2O, depicted in fig. 2.5. There are two special points in the phase diagram, however. One is the *triple point*, where the solid, liquid, and vapor (gas) phases all coexist. The second is the *critical point*, which is the terminus of the curve separating

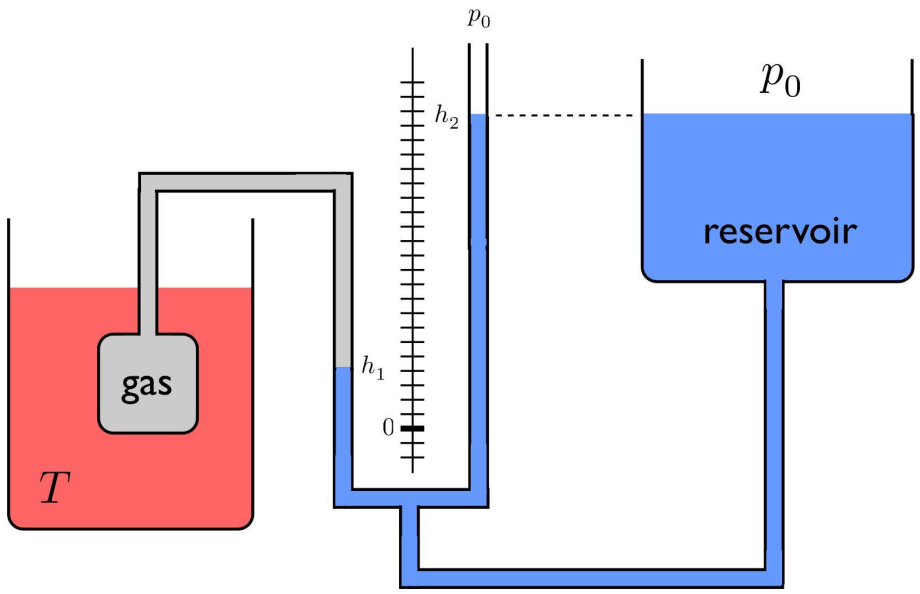


Figure 2.4: The constant volume gas thermometer. The gas is placed in thermal contact with an object of temperature T. An incompressible fluid of density ϱ is used to measure the pressure difference $\Delta p = p_{\rm gas} - p_0$.

liquid from gas. At the critical point, the *latent heat of transition* between liquid and gas phases vanishes (more on this later on). The triple point temperature $T_{\rm t}$ is thus *unique* and until 2019 was defined to be $T_{\rm t} = 273.16\,{\rm K}$. The pressure at the triple point is $611.7\,{\rm Pa} = 6.037 \times 10^{-3}\,{\rm atm}$. Since 2019, the kelvin has been defined by fixing Boltzmann's constant.

A question remains: are the two modes of the thermometer compatible? *E.g.* if we boil water at $p = p_0 = 1\,{\rm atm}$, do they yield the same value for T? And what if we use a different gas in our measurements? In fact, all these measurements will in general be *incompatible*, yielding different results for the temperature T. However, in the limit that we use a very low density gas, all the results converge. This is because all low density gases behave as *ideal gases*, and obey the ideal gas equation of state $pV = Nk_{\rm B}T$.

2.2.7 Standard temperature and pressure

It is customary in the physical sciences to define certain standard conditions with respect to which any arbitrary conditions may be compared. In thermodynamics, there is a notion of *standard temperature and pressure*, abbreviated STP. Unfortunately, there are two *different* definitions of STP currently in use, one from the International Union of Pure and Applied Chemistry (IUPAC), and the other from the U.S. National Institute of Standards and Technology (NIST). The two standards are:

$$\begin{aligned} {\rm IUPAC}\ &:\ T_0 = 0^\circ\,{\rm C} = 273.15\,{\rm K} \quad , \quad p_0 = 10^5\,{\rm Pa} \\ {\rm NIST}\ &:\ T_0 = 20^\circ\,{\rm C} = 293.15\,{\rm K} \quad , \quad p_0 = 1\,{\rm atm} = 1.01325 \times 10^5\,{\rm Pa} \end{aligned}$$

To make matters worse, in the past it was customary to define STP as $T_0 = 0^\circ\,{\rm C}$ and $p_0 = 1\,{\rm atm}$. We will use the NIST definition in this course. Unless I slip and use the IUPAC definition. Figuring out what I

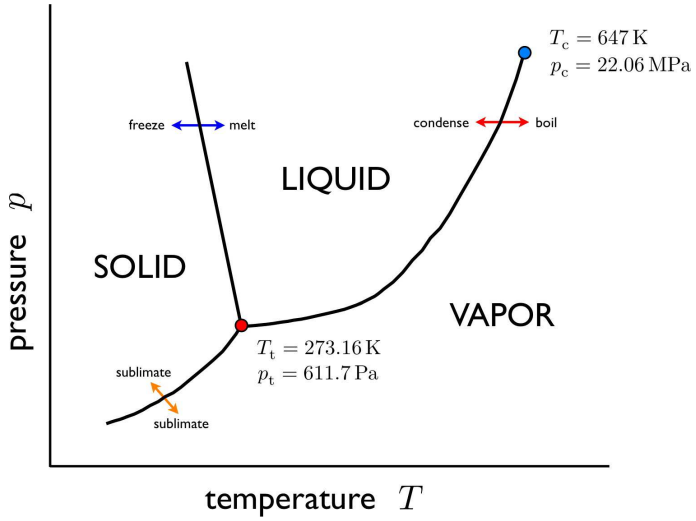


Figure 2.5: A sketch of the phase diagram of H_2O (water). Two special points are identified: the triple point (T_t, p_t) at which there is three phase coexistence, and the critical point (T_c, p_c), where the latent heat of transformation from liquid to gas vanishes. Not shown are transitions between several different solid phases.

mean by STP will keep you on your toes.

The volume of one mole of ideal gas at STP is then

$$V = \frac{N_A k_B T_0}{p_0} = \begin{cases} 22.711\ \ell & \text{(IUPAC)} \\ 24.219\ \ell & \text{(NIST)} \end{cases}, \tag{2.17}$$

where $1\,\ell = 10^3\,\mathrm{cm}^3 = 10^{-3}\,\mathrm{m}^3$ is one liter. Under the old definition of STP as $T_0 = 0^\circ\,\mathrm{C}$ and $p_0 = 1\,\mathrm{atm}$, the volume of one mole of gas at STP is $22.414\ \ell$, which is a figure I remember from my 10^{th} grade chemistry class with Mr. Lawrence.

2.3 The Zeroth Law of Thermodynamics

Equilibrium is established by the exchange of energy, volume, or particle number between different systems or subsystems:

$$\begin{aligned} &\text{energy exchange} &&\Longrightarrow &&T = \text{ constant} &&\Longrightarrow &&\text{thermal equilibrium} \\ &\text{volume exchange} &&\Longrightarrow &&\frac{p}{T} = \text{ constant} &&\Longrightarrow &&\text{mechanical equilibrium} \\ &\text{particle exchange} &&\Longrightarrow &&\frac{\mu}{T} = \text{ constant} &&\Longrightarrow &&\text{chemical equilibrium} \end{aligned}$$

Equilibrium is transitive, so

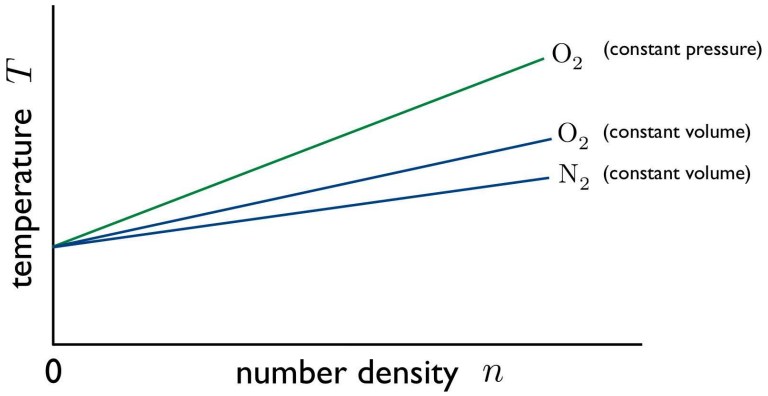


Figure 2.6: As the gas density tends to zero, the readings of the constant volume gas thermometer converge.

If A is in equilibrium with B, and B with C, then A is in equilibrium with C.

This is known as the Zeroth Law of Thermodynamics[6].

2.3.1 Gibbs phase rule

We see in fig. 2.5 that there are special lower-dimensional subsets of the phase diagram (*i.e.* curves and points) where different phases may *coexist* – a nongeneric state of affairs. For a system with c distinct components, $\mathsf{c}+2$ state variables are required for a complete specification of any equilibrium phase, at least one of which must be extensive. If we choose *only* one extensive variable, say the volume V, then we may construct a *phase diagram* where the axes correspond to the $\mathsf{c}+1$ quantities $\{T, p, \mu_1, \ldots, \mu_{\mathsf{c}-1}\}$. The Gibbs-Duhem relation (see eqn. 2.111) then guarantees that *any* intensive quantity ϕ may be expressed as a state function $\phi = \phi(T, p, \mu_1, \ldots, \mu_{\mathsf{c}-1})$. In particular, the $\mathsf{c}^{\rm th}$ chemical potential μ_{c} may be expressed as such a state function. The phase diagram doesn't depend on the extensive variable – H_2O at atmospheric pressure freezes at 0° C regardless of the amount of substance present.

As we shall derive in §2.11.5 below, a number φ distinct thermodynamic phases may coexist in a state of *phase equilibrium* throughout a $d(\mathsf{c}, \varphi) = \mathsf{c} + 2 - \varphi$ dimensional subset of the full $(\mathsf{c}+1)$-dimensional space $\Sigma = \{T, p, \mu_1, \ldots, \mu_{\mathsf{c}-1}\}$[7]. Since $d \geq 0$, we must have $\varphi \leq \mathsf{c} + 2$. Thus, for a single component ($\mathsf{c} = 1$) system like H_2O, we can have up to three-phase coexistence ($\varphi \leq 3$), as exemplified by the existence of a triple point in the phase diagram. There are also curves along which there is two-phase coexistence ($\varphi = 2$) between solid and liquid, liquid and gas, and solid and gas. Away from these special phase coexistence regions, full equilibrium entails that p, T, and μ are constant throughout the system. Furthermore, *all* intensive quantities, such as the specific volume $v = n^{-1}$ or energy density ε, are also

[6] As we shall see further below, thermomechanical equilibrium in fact leads to constant p/T, and thermochemical equilibrium to constant μ/T. If there is thermal equilibrium, then T is already constant, and so thermomechanical and thermochemical equilibria then guarantee the constancy of p and μ.

[7] Thus the codimension of the phase coexistence space is $\bar{d}(\mathsf{c}, \varphi) = \mathsf{c} + 1 - d(\mathsf{c}, \varphi) = \varphi - 1$. Thus for $\varphi = 1$ we have $\bar{d} = 0$.

constant. However, in the phase coexistence regions, this latter condition is no longer the case. Along the liquid-gas boundary, for example, the liquid and gas regions – in the presence of a gravitational field, the denser liquid component will separate out at the bottom – will have *different* specific volumes and energy densities.

2.4 The First Law of Thermodynamics

2.4.1 Conservation of energy

The first law is a statement of energy conservation, and is depicted in fig. 2.7. It says, quite simply, that during a thermodynamic process, the change in a system's internal energy E is given by the heat energy Q added *to* the system, minus the work W done *by* the system:

$$\Delta E = Q - W \quad . \tag{2.18}$$

The differential form of this, the First Law of Thermodynamics, is

$$dE = đQ - đW \quad . \tag{2.19}$$

We use the symbol $đ$ in the differentials $đQ$ and $đW$ to remind us that these are inexact differentials. The energy E, however, is a state function, hence dE is an exact differential.

Consider a volume V of fluid held in a flask, initially at temperature T_0, and held at atmospheric pressure. The internal energy is then $E_0 = E(T_0, p, V)$. Now let us contemplate changing the temperature in two different ways. The first method (A) is to place the flask on a hot plate until the temperature of the fluid rises to a value T_1. The second method (B) is to stir the fluid vigorously. In the first case, we add heat $Q_{\rm A} > 0$ but no work is done[8], so $W_{\rm A} = 0$. In the second case, if we thermally insulate the flask and use a stirrer of very low thermal conductivity, then no heat is added, *i.e.* $Q_{\rm B} = 0$. However, the stirrer does work $-W_{\rm B} > 0$ on the fluid (remember W is the work done by the system). If we end up at the same temperature T_1, then the final energy is $E_1 = E(T_1, p, V)$ in both cases. We then have

$$\Delta E = E_1 - E_0 = Q_{\rm A} = -W_{\rm B} \quad . \tag{2.20}$$

It also follows that for any cyclic transformation, where the state variables are the same at the beginning and the end, we have

$$\Delta E_{\rm cyclic} = Q - W = 0 \quad \Longrightarrow \quad Q = W \quad \text{(cyclic)} \quad . \tag{2.21}$$

2.4.2 Single component systems

A single component system is specified by three state variables. In many applications, the total number of particles N is conserved, so it is useful to take N as one of the state variables. The remaining two can

[8] In fact, the assumptions of constant pressure and zero work are inconsistent here. A fluid heated at atmospheric pressure generally will expand, so work $W_{\rm A} = p\,\Delta V$ is done. Typically this is a small amount if the fluid remains in its liquid state. More correctly, we can replace our flask with a rigid, closed vessel.

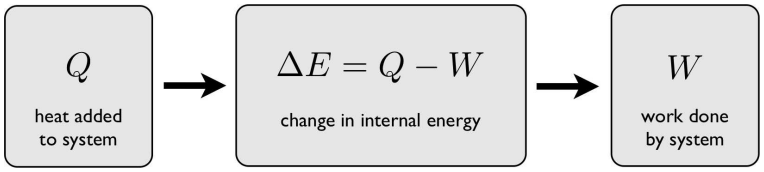


Figure 2.7: The first law of thermodynamics is a statement of energy conservation.

be (T, V) or (T, p) or (p, V). The differential form of the first law says

$$\begin{aligned} dE &= đQ - đW \\ &= đQ - p\,dV + \mu\,dN \quad . \end{aligned} \tag{2.22}$$

The quantity μ is called the *chemical potential*. We ask: how much heat is required in order to make an infinitesimal change in temperature, pressure, volume, or particle number? We start by rewriting eqn. 2.22 as

$$đQ = dE + p\,dV - \mu\,dN \quad . \tag{2.23}$$

We now must roll up our sleeves and do some work with partial derivatives.

• (T, V, N) systems : If the state variables are (T, V, N), we write

$$dE = \left(\frac{\partial E}{\partial T}\right)_{V,N} dT + \left(\frac{\partial E}{\partial V}\right)_{T,N} dV + \left(\frac{\partial E}{\partial N}\right)_{T,V} dN \quad . \tag{2.24}$$

Then

$$đQ = \left(\frac{\partial E}{\partial T}\right)_{V,N} dT + \left[\left(\frac{\partial E}{\partial V}\right)_{T,N} + p\right] dV + \left[\left(\frac{\partial E}{\partial N}\right)_{T,V} - \mu\right] dN \quad . \tag{2.25}$$

• (T, p, N) systems : If the state variables are (T, p, N), we write

$$dE = \left(\frac{\partial E}{\partial T}\right)_{p,N} dT + \left(\frac{\partial E}{\partial p}\right)_{T,N} dp + \left(\frac{\partial E}{\partial N}\right)_{T,p} dN \quad . \tag{2.26}$$

We also write

$$dV = \left(\frac{\partial V}{\partial T}\right)_{p,N} dT + \left(\frac{\partial V}{\partial p}\right)_{T,N} dp + \left(\frac{\partial V}{\partial N}\right)_{T,p} dN \quad . \tag{2.27}$$

Then

$$\begin{aligned} đQ = &\left[\left(\frac{\partial E}{\partial T}\right)_{p,N} + p\left(\frac{\partial V}{\partial T}\right)_{p,N}\right] dT + \left[\left(\frac{\partial E}{\partial p}\right)_{T,N} + p\left(\frac{\partial V}{\partial p}\right)_{T,N}\right] dp \\ &+ \left[\left(\frac{\partial E}{\partial N}\right)_{T,p} + p\left(\frac{\partial V}{\partial N}\right)_{T,p} - \mu\right] dN \quad . \end{aligned} \tag{2.28}$$

• (p, V, N) systems : If the state variables are (p, V, N), we write

$$dE = \left(\frac{\partial E}{\partial p}\right)_{V,N} dp + \left(\frac{\partial E}{\partial V}\right)_{p,N} dV + \left(\frac{\partial E}{\partial N}\right)_{p,V} dN \quad . \tag{2.29}$$

SUBSTANCE	c_p (J/mol K)	$\tilde{c}_p$ (J/g K)	SUBSTANCE	c_p (J/mol K)	$\tilde{c}_p$ (J/g K)
Air	29.07	1.01	H_2O (25° C)	75.34	4.181
Aluminum	24.2	0.897	H_2O (100°_+ C)	37.47	2.08
Copper	24.47	0.385	Iron	25.1	0.450
CO_2	36.94	0.839	Lead	26.4	0.127
Diamond	6.115	0.509	Lithium	24.8	3.58
Ethanol	112	2.44	Neon	20.786	1.03
Gold	25.42	0.129	Oxygen	29.38	0.918
Helium	20.786	5.193	Paraffin (wax)	900	2.5
Hydrogen	28.82	14.30	Uranium	27.7	0.116
H_2O (−10° C)	38.09	2.05	Zinc	25.3	0.387

Table 2.1: Specific heat (at 25° C, unless otherwise noted) of some common substances. (*Source: Wikipedia.*)

Then

$$đQ = \left(\frac{\partial E}{\partial p}\right)_{V,N} dp + \left[\left(\frac{\partial E}{\partial V}\right)_{p,N} + p\right] dV + \left[\left(\frac{\partial E}{\partial N}\right)_{p,V} - \mu\right] dN \quad . \tag{2.30}$$

2.4.3 Heat capacity

The *heat capacity* of a body, C, is by definition the ratio $đQ/dT$ of the amount of heat absorbed by the body to the associated infinitesimal change in temperature dT. The heat capacity will in general be different if the body is heated at constant volume or at constant pressure. Setting $dV = 0$ gives, from eqn. 2.25,

$$C_{V,N} = \left(\frac{đQ}{dT}\right)_{V,N} = \left(\frac{\partial E}{\partial T}\right)_{V,N} \quad . \tag{2.31}$$

Similarly, if we set $dp = 0$, then eqn. 2.28 yields

$$C_{p,N} = \left(\frac{đQ}{dT}\right)_{p,N} = \left(\frac{\partial E}{\partial T}\right)_{p,N} + p\left(\frac{\partial V}{\partial T}\right)_{p,N} \quad . \tag{2.32}$$

Unless otherwise stated, we shall assume that N is fixed, and will write C_V for $C_{V,N}$ and C_p for $C_{p,N}$.

The units of heat capacity are energy divided by temperature, *e.g.* J/K. The heat capacity is an extensive quantity, scaling with the size of the system. If we divide by the number of moles $N/N_{\rm A}$, we obtain the *molar heat capacity*, sometimes called the *molar specific heat*: $c = C/\nu$, where $\nu = N/N_{\rm A}$ is the number of moles of substance. Specific heat is also sometimes quoted in units of heat capacity per gram of

substance. We shall define

$$\tilde{c} = \frac{C}{mN} = \frac{c}{M} = \frac{\text{heat capacity per mole}}{\text{mass per mole}} \quad . \tag{2.33}$$

Here m is the mass per particle and M is the mass per mole: $M = N_{\rm A}\, m$.

Suppose we raise the temperature of a body from $T = T_{\rm A}$ to $T = T_{\rm B}$. How much heat is required? We have

$$Q = \int\limits_{T_{\rm A}}^{T_{\rm B}} dT\, C(T) \quad , \tag{2.34}$$

where $C = C_V$ or $C = C_p$ depending on whether volume or pressure is held constant. For ideal gases with no internal degrees of freedom, as we shall discuss below, $C(T)$ is constant, and thus

$$Q = C(T_{\rm B} - T_{\rm A}) \quad \Longrightarrow \quad T_{\rm B} = T_{\rm A} + \frac{Q}{C} \quad . \tag{2.35}$$

In metals at very low temperatures one finds $C = \gamma T$, where γ is a constant[9]. We then have

$$Q = \int\limits_{T_{\rm A}}^{T_{\rm B}} dT\, C(T) = \tfrac{1}{2}\gamma\big(T_{\rm B}^2 - T_{\rm A}^2\big) \quad \Longrightarrow \quad T_{\rm B} = \sqrt{T_{\rm A}^2 + 2\gamma^{-1}Q} \quad . \tag{2.36}$$

Calorimetry

We measure specific heat using a device called a *calorimeter*, of which there are many types. The basic physics is that a substance initially in equilibrium at temperature T_1 put in thermal contact with a reference fluid (typically H_2O) in equilibrium at temperature $T_2 > T_1$ will come to equilibrium at some final temperature $T_{\rm f} \in (T_1, T_2)$. If the substance and the reference fluid are thermally isolated from the rest of the universe, then the heat energy gained by the solid is the heat energy lost by the reference fluid. Assuming the specific heats $\tilde{c}_{\rm s,r}(T)$ are constant throughout the regime $T \in [T_1, T_2]$, we then have

$$Q = M_{\rm s}\,\tilde{c}_{\rm s}\cdot(T_{\rm f} - T_1) = M_{\rm r}\,\tilde{c}_{\rm r}\cdot(T_2 - T_{\rm f}) \quad \Rightarrow \quad \tilde{c}_{\rm s} = \frac{M_{\rm r}}{M_{\rm s}}\cdot\frac{T_2 - T_{\rm f}}{T_{\rm f} - T_1} \quad . \tag{2.37}$$

Thus, a measurement of the final temperature $T_{\rm f}$ can be used to determine the unknown $\tilde{c}_{\rm s}$. For H_2O, it requires $4.1855\,\mathrm{J}$ per gram of energy to raise the temperature from $T = 14.5^\circ\mathrm{C}$ to $T' = 15.5^\circ\mathrm{C}$, which is to say $\tilde{c}_{\rm H_2O}(T = 15^\circ\mathrm{C}) = 4.1855\,\mathrm{J/g\,^\circ C}$.[10] In practice, the fluid is contained in a vessel which has its own heat capacity and which must be accounted for in the determination of $\tilde{c}_{\rm s}$.

[9] In most metals, the difference between C_V and C_p is negligible.

[10] The specific heat $\tilde{c}_{\rm H_2O}(T)$ is weakly temperature dependent throughout much of the liquid phase. It turns out that $\tilde{c}_{\rm H_2O}(T = 20^\circ\mathrm{C}) = 4.1819\,\mathrm{J/g\,^\circ C}$. The conversion factor between Joules and *thermochemical calories* is $1\,\mathrm{J} = 0.2390\,\mathrm{cal}$. The so-called "15° calorie" is equivalent to 4.1855 Joules.

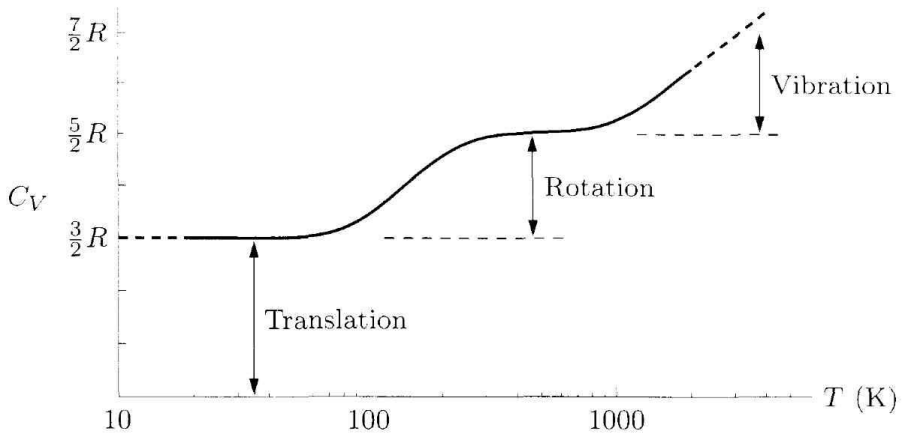


Figure 2.8: Heat capacity C_V for one mole of hydrogen (H_2) gas. At the lowest temperatures, only translational degrees of freedom are relevant, and $f = 3$. At around 200 K, two rotational modes are excitable and $f = 5$. Above 1000 K, the vibrational excitations begin to contribute. Note the logarithmic temperature scale. (Data from H. W. Wooley *et al.*, *Jour. Natl. Bureau of Standards*, **41**, 379 (1948).)

2.4.4 Ideal gases

The ideal gas equation of state is $pV = Nk_{\rm B}T$. In order to invoke the formulae in eqns. 2.25, 2.28, and 2.30, we need to know the state function $E(T, V, N)$. A landmark experiment by Joule in the mid-19th century established that the energy of a low density gas is independent of its volume[11]. Essentially, a gas at temperature T was allowed to freely expand from one volume V to a larger volume $V' > V$, with no added heat Q and no work W done. Therefore the energy cannot change. What Joule found was that the temperature also did not change. This means that $E(T, V, N) = E(T, N)$ cannot be a function of the volume.

Since E is extensive, we conclude that

$$E(T, V, N) = \nu\,\varepsilon(T) \quad , \tag{2.38}$$

where $\nu = N/N_{\rm A}$ is the number of moles of substance. Note that ν is an extensive variable. From eqns. 2.31 and 2.32, we conclude

$$C_V(T) = \nu\,\varepsilon'(T) \qquad , \qquad C_p(T) = C_V(T) + \nu R \quad , \tag{2.39}$$

where we invoke the ideal gas law to obtain the second of these. Empirically it is found that $C_V(T)$ is temperature independent over a wide range of T, far enough from boiling point. We can then write $C_V = \nu\, c_V$, where $\nu \equiv N/N_{\rm A}$ is the number of moles, and where c_V is the molar heat capacity. We then have $c_p = c_V + R$, where $R = N_{\rm A}k_{\rm B} = 8.314462618\,{\rm J/mol\,K}$ is the *gas constant*. We denote by $\gamma = c_p/c_V$ the ratio of specific heat at constant pressure and at constant volume.

[11] See the description in E. Fermi, *Thermodynamics*, pp. 22-23.

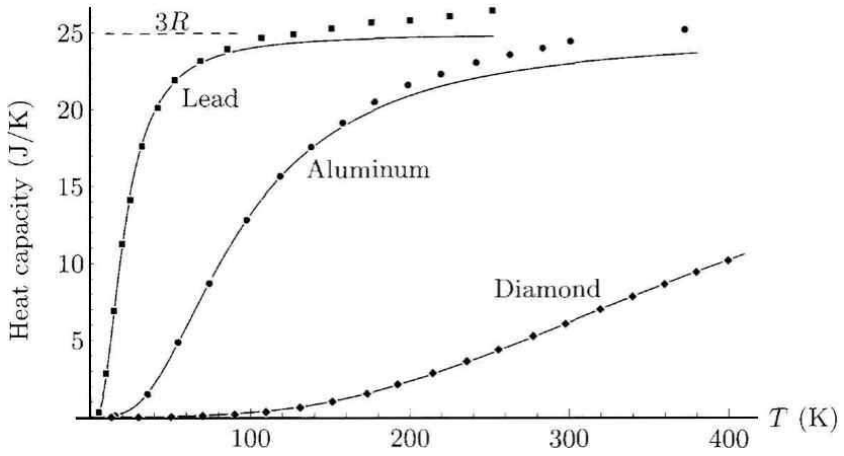


Figure 2.9: Molar heat capacities c_V for three solids. The solid curves correspond to the predictions of the Debye model, which we shall discuss later.

From the kinetic theory of gases, one can show that

$$\begin{aligned} \text{monatomic gases:} \quad & c_V = \tfrac{3}{2}R \quad , \quad c_p = \tfrac{5}{2}R \quad , \quad \gamma = \tfrac{5}{3} \\ \text{diatomic gases:} \quad & c_V = \tfrac{5}{2}R \quad , \quad c_p = \tfrac{7}{2}R \quad , \quad \gamma = \tfrac{7}{5} \\ \text{polyatomic gases:} \quad & c_V = 3R \quad , \quad c_p = 4R \quad , \quad \gamma = \tfrac{4}{3} \quad . \end{aligned}$$

In the polyatomic case we assume the molecule is not linear; linear molecules, even if polyatomic, have only two rotational modes for the same reason that diatomic molecules do, *i.e.* the rotational inertial about their axis is so small that the associated quantized rotational energy levels are typically well above thermal energy scales. For linear polyatomic molecules, $f = 5$.

Digression : kinetic theory of gases

We will conclude in general from noninteracting classical statistical mechanics that the specific heat of a substance is $c_v = \frac{1}{2}fR$, where f is the number of phase space coordinates, per particle, for which there is a quadratic kinetic or potential energy function. For example, a point particle has three translational degrees of freedom, and the kinetic energy is a quadratic function of their conjugate momenta: $H_0 = (p_x^2 + p_y^2 + p_z^2)/2m$. Thus, $f = 3$. Diatomic molecules have two additional rotational degrees of freedom – we don't count rotations about the symmetry axis – and their conjugate momenta also appear quadratically in the kinetic energy, leading to $f = 5$. For polyatomic molecules, all three Euler angles and their conjugate momenta are in play, and $f = 6$.

The reason that $f = 5$ for diatomic molecules rather than $f = 6$ is due to quantum mechanics. While translational eigenstates form a continuum, or are quantized in a box with $\Delta k_\alpha = 2\pi/L_\alpha$ being very small, since the dimensions L_α are macroscopic, angular momentum, and hence rotational kinetic energy, is quantized. For rotations about a principal axis with very low moment of inertia I, the corresponding energy scale $\hbar^2/2I$ is very large, and a high temperature is required in order to thermally populate these states. Thus, degrees of freedom with a quantization energy on the order of or greater than ε_0 are 'frozen out' for temperatures $T \lesssim \varepsilon_0/k_{\rm B}$.

In solids, each atom is effectively connected to its neighbors by springs; such a potential arises from quantum mechanical and electrostatic consideration of the interacting atoms. Thus, each degree of freedom contributes to the potential energy, and its conjugate momentum contributes to the kinetic energy. This results in $f = 6$. Assuming only lattice vibrations, then, the high temperature limit for $c_V(T)$ for any solid is predicted to be $3R = 24.944\,\mathrm{J/mol\,K}$. This is called the *Dulong-Petit law*. The high temperature limit is reached above the so-called *Debye temperature*, which is roughly proportional to the melting temperature of the solid.

In table 2.1, we list c_p and $\tilde{c}_p$ for some common substances at $T = 25^\circ\,\mathrm{C}$ (unless otherwise noted). Note that c_p for the monatomic gases He and Ne is to high accuracy given by the value from kinetic theory, $c_p = \frac{5}{2}R = 20.7864\,\mathrm{J/mol\,K}$. For the diatomic gases oxygen (O_2) and air (mostly N_2 and O_2), kinetic theory predicts $c_p = \frac{7}{2}R = 29.10$, which is close to the measured values. Kinetic theory predicts $c_p = 4R = 33.258$ for polyatomic gases; the measured values for CO_2 and H_2O are both about 10% higher.

2.4.5 Adiabatic transformations of ideal gases

Assuming $dN = 0$ and $E = \nu\,\varepsilon(T)$, eqn. 2.25 tells us that

$$đQ = C_V\,dT + p\,dV \quad . \tag{2.40}$$

Invoking the ideal gas law to write $p = \nu RT/V$, and remembering $C_V = \nu\,c_V$, we have, setting $đQ = 0$,

$$\frac{dT}{T} + \frac{R}{c_V}\frac{dV}{V} = 0 \quad . \tag{2.41}$$

We can immediately integrate to obtain

$$đQ = 0 \quad \Longrightarrow \quad \begin{cases} TV^{\gamma-1} = \text{constant} \\ pV^{\gamma} = \text{constant} \\ T^{\gamma}p^{1-\gamma} = \text{constant} \end{cases} \tag{2.42}$$

where the second two equations are obtained from the first by invoking the ideal gas law. These are all *adiabatic equations of state*. Note the difference between the adiabatic equation of state $d(pV^\gamma) = 0$ and the isothermal equation of state $d(pV) = 0$. Equivalently, we can write these three conditions as

$$V^2\,T^f = V_0^2\,T_0^f \qquad , \qquad p^f\,V^{f+2} = p_0^f\,V_0^{f+2} \qquad , \qquad T^{f+2}\,p^{-2} = T_0^{f+2}\,p_0^{-2} \quad . \tag{2.43}$$

It turns out that air is a rather poor conductor of heat. This suggests the following model for an *adiabatic atmosphere*. The hydrostatic pressure decrease associated with an increase dz in height is $dp = -\varrho g\,dz$, where ϱ is the density and g the acceleration due to gravity. Assuming the gas is ideal, the density can be written as $\varrho = Mp/RT$, where M is the molar mass. Thus,

$$\frac{dp}{p} = -\frac{Mg}{RT}\,dz \quad . \tag{2.44}$$

If the atmosphere is isothermal, then T is constant and $p(z) = p(0)\exp(-z/\lambda)$, where $\lambda = RT/Mg$. This also entails an exponential profile of the density: $\varrho(z) = \varrho(0)\,\exp(-z/\lambda)$. With $M = 28.88\,\mathrm{g}$ for air and $T = 293\,\mathrm{K}$, we have $\lambda = 8.6\,\mathrm{km}$.

If, on the other hand, the atmosphere is adiabatic, then from $d(T^\gamma p^{1-\gamma}) = 0$, we have

$$dT = \frac{\gamma-1}{\gamma}\,\frac{Tdp}{p} = -\frac{\gamma-1}{\gamma}\,\frac{Mg}{R}\,dz \quad , \tag{2.45}$$

with the solution

$$T(z) = T_0 - \frac{\gamma-1}{\gamma}\,\frac{Mg}{R}\,z = \left(1 - \frac{\gamma-1}{\gamma}\,\frac{z}{\lambda}\right)T_0 \quad , \tag{2.46}$$

where $T_0 = T(0) = 293\,\mathrm{K}$ is the temperature at the earth's surface, and $\lambda = RT_0/Mg$ as above. Air is mostly diatomic, and taking $\gamma = \frac{7}{5}$ we obtain $dT/dz = -(1-\gamma^{-1})\,T_0/\lambda = -9.7\,\mathrm{K/km}$. Note that in this model the atmosphere ends at a height $z_{\max} = \gamma\lambda/(\gamma-1) = 30\,\mathrm{km}$.

Again invoking the adiabatic equation of state, we can find $p(z)$:

$$\frac{p(z)}{p_0} = \left(\frac{T}{T_0}\right)^{\frac{\gamma}{\gamma-1}} = \left(1 - \frac{\gamma-1}{\gamma}\,\frac{z}{\lambda}\right)^{\frac{\gamma}{\gamma-1}} \tag{2.47}$$

Since $\varrho \propto p/T$ from the ideal gas law, we have

$$\frac{\varrho(z)}{\varrho_0} = \left(1 - \frac{\gamma-1}{\gamma}\,\frac{z}{\lambda}\right)^{\frac{1}{\gamma-1}} \quad . \tag{2.48}$$

Finally, recall the mathematical result $e^x = \lim_{k\to\infty}\left(1+\frac{x}{k}\right)^k$. Thus, in the limit $\gamma \to 1$, where $k = \gamma/(\gamma-1) \to \infty$, we recover the isothermal result $p(z) = p_0\,\exp(-z/\lambda)$. This makes sense because $d(T^\gamma p^{1-\gamma}) = dT = 0$ for $\gamma = 1$.

2.4.6 Adiabatic free expansion

Consider the situation depicted in fig. 2.10. A quantity (ν moles) of gas in equilibrium at temperature T and volume V_1 is allowed to expand freely into an evacuated chamber of volume V_2 by the removal of a barrier. Clearly no work is done on or by the gas during this process, hence $W = 0$. If the walls are everywhere insulating, so that no heat can pass through them, then $Q = 0$ as well. The First Law then gives $\Delta E = Q - W = 0$, and there is no change in energy.

If the gas is ideal, then since $E(T,V,N) = \nu c_V T$ with $\nu = N/N_{\mathrm{A}}$, $\Delta E = 0$ gives $\Delta T = 0$, and there is no change in temperature. (If the walls are insulating against the passage of heat, they must also prevent the passage of particles, so $\Delta N = 0$.) There is of course a change in volume: $\Delta V = V_2$, hence there is a change in pressure. The initial pressure is $p = Nk_{\mathrm{B}}T/V_1$ and the final pressure is $p' = Nk_{\mathrm{B}}T/(V_1+V_2)$.

If the gas is nonideal, then the temperature will in general change. Suppose $E(T,V,N) = \alpha\,V^x\,N^{1-x}\,T^y$, where α, x, and y are constants. This form is properly extensive: if V and N double, then E doubles. If the volume changes from V to V' under an adiabatic free expansion, then we must have, from $\Delta E = 0$,

$$\left(\frac{V}{V'}\right)^x = \left(\frac{T'}{T}\right)^y \qquad \Longrightarrow \qquad T' = T\cdot\left(\frac{V}{V'}\right)^{x/y} \quad . \tag{2.49}$$

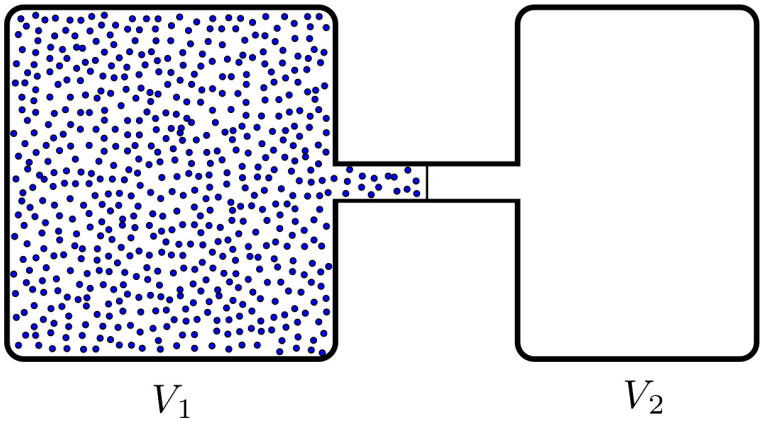


Figure 2.10: In the adiabatic free expansion of a gas, there is volume expansion with no work or heat exchange with the environment: $\Delta E = Q = W = 0$.

If $x/y > 0$, the temperature decreases upon the expansion. If $x/y < 0$, the temperature increases. Without an equation of state, we can't say precisely what happens to the pressure. Does the pressure decrease? Not necessarily! While thermodynamic stability entails a positive isothermal compressibility $\kappa_T = -V^{-1}(\partial V/\partial p)_{T,N} > 0$, thermodynamics does not impose a universal sign on $(\partial p/\partial V)_{E,N}$.

Adiabatic free expansion of a gas is a *spontaneous process*, arising due to the natural internal dynamics of the system. It is also *irreversible*. If we wish to take the gas back to its original state, we must do work on it to compress it. If the gas is ideal, then the initial and final temperatures are identical, so we can place the system in thermal contact with a reservoir at temperature T and follow a thermodynamic path along an isotherm. The work done *on the gas* during compression is then

$$\mathcal{W} = -Nk_{\rm B}T \int_{V_{\rm f}}^{V_{\rm i}} \frac{dV}{V} = Nk_{\rm B}T \, \log\left(\frac{V_{\rm f}}{V_{\rm i}}\right) = Nk_{\rm B}T \, \log\left(1 + \frac{V_2}{V_1}\right) \quad . \tag{2.50}$$

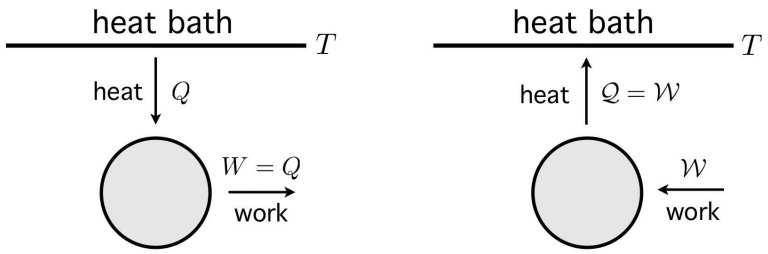
The work done *by the gas* is $W = \int p\, dV = -\mathcal{W}$. During the compression, heat energy $Q = W < 0$ is transferred to the gas from the reservoir. Thus, $\mathcal{Q} = \mathcal{W} > 0$ is given off by the gas to its environment.

2.5 Heat Engines and the Second Law of Thermodynamics

2.5.1 There's no free lunch so quit asking

A *heat engine* is a device which takes a thermodynamic system through a repeated cycle which can be represented as a succession of equilibrium states: $\mathrm{A} \to \mathrm{B} \to \mathrm{C} \cdots \to \mathrm{A}$. The net result of such a cyclic process is to convert heat into mechanical work, or *vice versa*.

For a system in equilibrium at temperature T, there is a thermodynamically large amount of internal energy stored in the random internal motion of its constituent particles. Later, when we study statistical mechanics, we will see how each 'quadratic' degree of freedom in the Hamiltonian contributes $\frac{1}{2}k_{\rm B}T$



(a) a perfect engine (b) a perfect waste of time

Figure 2.11: A *perfect engine* would extract heat Q from a thermal reservoir at some temperature T and convert it into useful mechanical work W. This process is alas impossible, according to the Second Law of thermodynamics. The inverse process, where work $\mathcal{W}$ is converted into heat $\mathcal{Q}$, is always possible.

to the total internal energy. An immense body in equilibrium at temperature T has an enormous heat capacity C, so extracting a finite quantity of heat Q from it results in a temperature change $\Delta T = -Q/C$ which is utterly negligible. Such a body is called a *heat bath*, or *thermal reservoir*. A *perfect engine* would, in each cycle, extract an amount of heat Q from the bath and convert it into work. Since $\Delta E = 0$ for a cyclic process, the First Law then gives $W = Q$. This situation is depicted schematically in fig. 2.11. One could imagine running this process virtually indefinitely, slowly sucking energy out of an immense heat bath, converting the random thermal motion of its constituent molecules into useful mechanical work. Sadly, this is not possible:

> *A transformation whose only final result is to extract heat from a source at fixed temperature and transform that heat into work is impossible.*

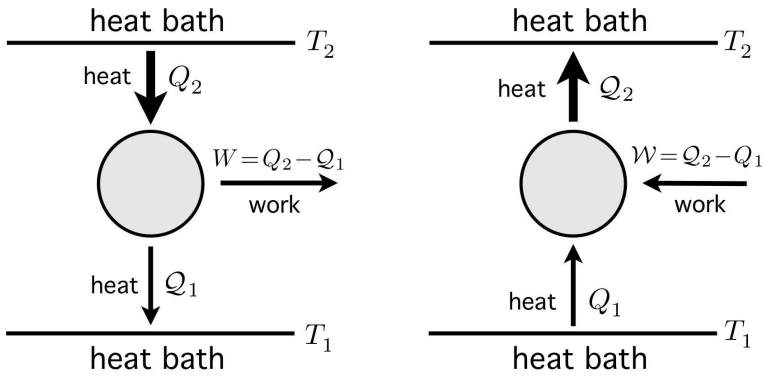
This is known as the *Postulate of Lord Kelvin*. It is equivalent to the *postulate of Clausius*,

> *A transformation whose only result is to transfer heat from a body at a given temperature to a body at higher temperature is impossible.*

These postulates which have been repeatedly validated by empirical observations, constitute the Second Law of Thermodynamics.

2.5.2 Engines and refrigerators

While it is not possible to convert heat into work with 100% efficiency, it is possible to transfer heat from one thermal reservoir to another one, at lower temperature, and to convert some of that heat into work. This is what an engine does. The energy accounting for one cycle of the engine is depicted in the left hand panel of fig. 2.12. An amount of heat $Q_2 > 0$ is extracted from the reservoir at temperature T_2. Since the reservoir is assumed to be enormous, its temperature change $\Delta T_2 = -Q_2/C_2$ is negligible, and its temperature remains constant – this is what it means for an object to be a reservoir. A lesser amount of heat, $\mathcal{Q}_1$, with $0 < \mathcal{Q}_1 < Q_2$, is deposited in a second reservoir at a lower temperature T_1. Its temperature change $\Delta T_1 = +\mathcal{Q}_1/C_1$ is also negligible. The difference $W = Q_2 - \mathcal{Q}_1$ is extracted as



(a) engine (b) refrigerator

Figure 2.12: An engine (left) extracts heat Q_2 from a reservoir at temperature T_2 and deposits a smaller amount of heat $\mathcal{Q}_1$ into a reservoir at a lower temperature T_1, during each cycle. The difference $W = Q_2 - \mathcal{Q}_1$ is transformed into mechanical work. A refrigerator (right) performs the inverse process, drawing heat Q_1 from a low temperature reservoir and depositing heat $\mathcal{Q}_2 = Q_1 + \mathcal{W}$ into a high temperature reservoir, where $\mathcal{W}$ is the mechanical (or electrical) work done per cycle.

useful work. We define the *efficiency*, η, of the engine as the ratio of the work done to the heat extracted from the upper reservoir, per cycle:

$$\eta = \frac{W}{Q_2} = 1 - \frac{\mathcal{Q}_1}{Q_2} \quad . \tag{2.51}$$

This is a natural definition of efficiency, since it will cost us fuel to maintain the temperature of the upper reservoir over many cycles of the engine. Thus, the efficiency is proportional to the ratio of the work done to the cost of the fuel.

A refrigerator works according to the same principles, but the process runs in reverse. An amount of heat Q_1 is extracted from the lower reservoir – the inside of our refrigerator – and is pumped into the upper reservoir. As Clausius' form of the Second Law asserts, it is impossible for this to be the only result of our cycle. Some amount of work $\mathcal{W}$ must be performed on the refrigerator in order for it to extract the heat Q_1. Since $\Delta E = 0$ for the cycle, a heat $\mathcal{Q}_2 = \mathcal{W} + Q_1$ must be deposited into the upper reservoir during each cycle. The analog of efficiency here is called the *coefficient of refrigeration*, κ, defined as

$$\kappa = \frac{Q_1}{\mathcal{W}} = \frac{Q_1}{\mathcal{Q}_2 - Q_1} \quad . \tag{2.52}$$

Thus, κ is proportional to the ratio of the heat extracted to the cost of electricity, per cycle.

Please note the deliberate notation here. I am using symbols Q and W to denote the heat supplied *to* the engine (or refrigerator) and the work done *by* the engine, respectively, and $\mathcal{Q}$ and $\mathcal{W}$ to denote the heat taken *from* the engine and the work done *on* the engine.

A perfect engine has $\mathcal{Q}_1 = 0$ and $\eta = 1$; a perfect refrigerator has $Q_1 = \mathcal{Q}_2$ and $\kappa = \infty$. Both violate the Second Law. Sadi Carnot[12] (1796 – 1832) realized that a *reversible* cyclic engine operating between

[12]Carnot died during the cholera epidemic of 1832. His is one of the 72 names engraved on the Eiffel Tower.

two thermal reservoirs must produce the maximum amount of work W, and that the amount of work produced is *independent of the material properties of the engine*. We call any such engine a *Carnot engine*.

The efficiency of a Carnot engine may be used to define a temperature scale. We know from Carnot's observations that the efficiency $\eta_{\rm C}$ can only be a function of the temperatures T_1 and T_2: $\eta_{\rm C} = \eta_{\rm C}(T_1, T_2)$. We can then define

$$\frac{T_1}{T_2} \equiv 1 - \eta_{\rm C}(T_1, T_2) \quad . \tag{2.53}$$

Below, in §2.5.4, we will see how, using an ideal gas as the 'working substance' of the Carnot engine, this temperature scale coincides precisely with the ideal gas temperature scale from §2.2.6.

2.5.3 Nothing beats a Carnot engine

The Carnot engine is the most efficient engine possible operating between two thermal reservoirs. To see this, let's suppose that an amazing wonder engine has an efficiency even greater than that of the Carnot engine. A key feature of the Carnot engine is its reversibility – we can just go around its cycle in the opposite direction, creating a Carnot refrigerator. Let's use our notional wonder engine to drive a Carnot refrigerator, as depicted in fig. 2.13.

We assume that

$$\frac{W}{Q_2} = \eta_{\rm wonder} > \eta_{\rm Carnot} = \frac{\mathcal{W}'}{\mathcal{Q}_2'} \quad . \tag{2.54}$$

But from the figure, we have $W = \mathcal{W}'$, and therefore the heat energy $\mathcal{Q}_2' - Q_2$ transferred *to* the upper reservoir is positive. From

$$W = Q_2 - \mathcal{Q}_1 = \mathcal{Q}_2' - Q_1' = \mathcal{W}' \quad , \tag{2.55}$$

we see that this is equal to the heat energy extracted *from* the lower reservoir, since no external work is done on the system:

$$\mathcal{Q}_2' - Q_2 = Q_1' - \mathcal{Q}_1 > 0 \quad . \tag{2.56}$$

Therefore, the existence of the wonder engine entails a violation of the Second Law. Since the Second Law is correct – *Lord* Kelvin articulated it, and who are we to argue with a *Lord*? – the wonder engine cannot exist.

We further conclude that *all reversible engines running between two thermal reservoirs have the same efficiency, which is the efficiency of a Carnot engine.* In general, we have

$$\eta = \frac{W}{Q_2} = 1 - \frac{\mathcal{Q}_1}{Q_2} \le 1 - \frac{T_1}{T_2} = \eta_{\rm C} \quad , \tag{2.57}$$

and therefore

$$\frac{Q_2}{T_2} - \frac{\mathcal{Q}_1}{T_1} \le 0 \quad , \tag{2.58}$$

with the equalities holding only for reversible engines.

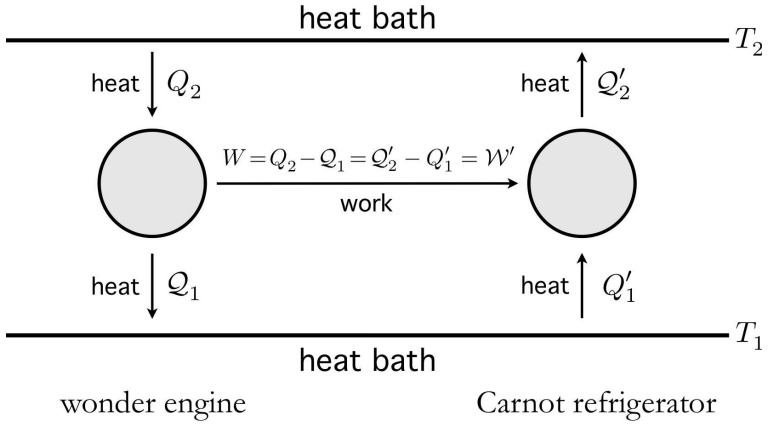


Figure 2.13: A wonder engine driving a Carnot refrigerator.

2.5.4 The Carnot cycle

Let us now consider a specific cycle, known as the Carnot cycle, depicted in fig. 2.14. The cycle consists of two adiabats and two isotherms. The work done per cycle is simply the area inside the curve on our $p - V$ diagram:

$$W = \oint p\, dV \quad . \tag{2.59}$$

The gas inside our Carnot engine is called the 'working substance'. Whatever it may be, the system obeys the First Law,

$$dE = đQ - đW = đQ - p\, dV \quad . \tag{2.60}$$

We will now assume that the working material is an ideal gas, and we compute W as well as $\mathcal{Q}_1$ and Q_2 to find the efficiency of this cycle. In order to do this, we will rely upon the ideal gas equations,

$$E = \frac{\nu RT}{\gamma - 1} \qquad , \qquad pV = \nu RT \quad , \tag{2.61}$$

where $\gamma = c_p/c_v = 1 + \frac{2}{f}$, where f is the effective number of molecular degrees of freedom contributing to the internal energy. Recall $f = 3$ for monatomic gases, $f = 5$ for diatomic gases, and $f = 6$ for polyatomic gases. The finite difference form of the first law is

$$\Delta E = E_{\rm f} - E_{\rm i} = Q_{\rm if} - W_{\rm if} \quad , \tag{2.62}$$

where i denotes the initial state and f the final state.

AB: This stage is an isothermal expansion at temperature T_2. It is the 'power stroke' of the engine. We have

$$W_{\rm AB} = \int_{V_{\rm A}}^{V_{\rm B}} dV\, \frac{\nu RT_2}{V} = \nu RT_2\, \log\left(\frac{V_{\rm B}}{V_{\rm A}}\right) \tag{2.63}$$

$$E_{\rm A} = E_{\rm B} = \frac{\nu RT_2}{\gamma - 1} \quad , \tag{2.64}$$

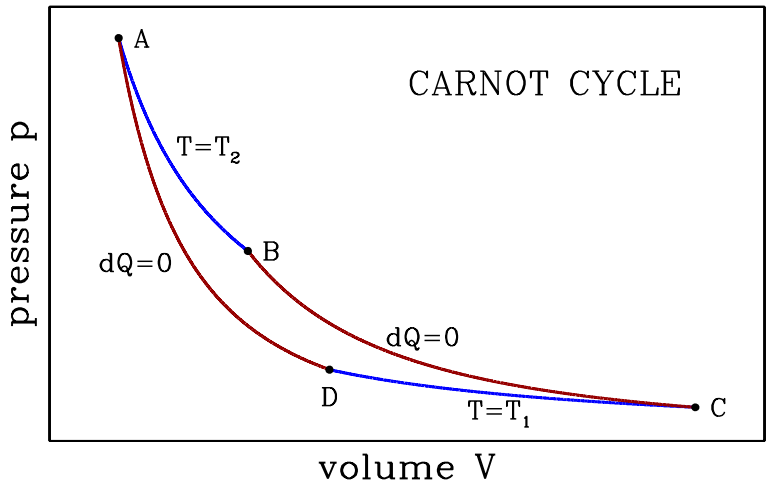


Figure 2.14: The Carnot cycle consists of two adiabats (dark red) and two isotherms (blue).

hence

$$Q_{\rm AB} = \Delta E_{\rm AB} + W_{\rm AB} = \nu R T_2 \, \log\left(\frac{V_{\rm B}}{V_{\rm A}}\right) \quad . \tag{2.65}$$

BC: This stage is an adiabatic expansion. We have

$$Q_{\rm BC} = 0 \tag{2.66}$$

$$\Delta E_{\rm BC} = E_{\rm C} - E_{\rm B} = \frac{\nu R}{\gamma - 1}\,(T_1 - T_2) \quad . \tag{2.67}$$

The energy change is negative, and the heat exchange is zero, so the engine still does some work during this stage:

$$W_{\rm BC} = Q_{\rm BC} - \Delta E_{\rm BC} = \frac{\nu R}{\gamma - 1}\,(T_2 - T_1) \quad . \tag{2.68}$$

CD: This stage is an isothermal compression, and we may apply the analysis of the isothermal expansion, *mutatis mutandis*:

$$W_{\rm CD} = \int_{V_{\rm C}}^{V_{\rm D}} dV \, \frac{\nu R T_1}{V} = \nu R T_1 \, \log\left(\frac{V_{\rm D}}{V_{\rm C}}\right) \tag{2.69}$$

$$E_{\rm C} = E_{\rm D} = \frac{\nu R T_1}{\gamma - 1} \quad , \tag{2.70}$$

hence

$$Q_{\rm CD} = \Delta E_{\rm CD} + W_{\rm CD} = \nu R T_1 \, \log\left(\frac{V_{\rm D}}{V_{\rm C}}\right) \quad . \tag{2.71}$$

DA: This last stage is an adiabatic compression, and we may draw on the results from the adiabatic

expansion in BC:

$$Q_{\rm DA} = 0 \tag{2.72}$$

$$\Delta E_{\rm DA} = E_{\rm A} - E_{\rm D} = \frac{\nu R}{\gamma - 1}\,(T_2 - T_1) \quad . \tag{2.73}$$

The energy change is positive, and the heat exchange is zero, so work is done on the engine:

$$W_{\rm DA} = Q_{\rm DA} - \Delta E_{\rm DA} = \frac{\nu R}{\gamma - 1}\,(T_1 - T_2) \quad . \tag{2.74}$$

We now add up all the work values from the individual stages to get for the cycle

$$\begin{aligned} W &= W_{\rm AB} + W_{\rm BC} + W_{\rm CD} + W_{\rm DA} \\ &= \nu R T_2\,\log\left(\frac{V_{\rm B}}{V_{\rm A}}\right) + \nu R T_1\,\log\left(\frac{V_{\rm D}}{V_{\rm C}}\right) \quad . \end{aligned} \tag{2.75}$$

Since we are analyzing a cyclic process, we must have $\Delta E = 0$, hence $Q = W$, which can of course be verified explicitly, by computing $Q = Q_{\rm AB} + Q_{\rm BC} + Q_{\rm CD} + Q_{\rm DA}$. To finish up, recall the adiabatic ideal gas equation of state, $d(TV^{\gamma-1}) = 0$. This tells us that

$$T_2\,V_{\rm B}^{\gamma-1} = T_1\,V_{\rm C}^{\gamma-1} \tag{2.76}$$

$$T_2\,V_{\rm A}^{\gamma-1} = T_1\,V_{\rm D}^{\gamma-1} \quad . \tag{2.77}$$

Dividing these two equations, we find

$$\frac{V_{\rm B}}{V_{\rm A}} = \frac{V_{\rm C}}{V_{\rm D}} \quad , \tag{2.78}$$

and therefore

$$W = \nu R(T_2 - T_1)\,\log\left(\frac{V_{\rm B}}{V_{\rm A}}\right) \tag{2.79}$$

$$Q_{\rm AB} = \nu R T_2\,\log\left(\frac{V_{\rm B}}{V_{\rm A}}\right) \quad . \tag{2.80}$$

Finally, the efficiency is given by the ratio of these two quantities:

$$\eta = \frac{W}{Q_{\rm AB}} = 1 - \frac{T_1}{T_2} \quad . \tag{2.81}$$

Examples of other useful thermodynamic cycles are discussed in the appendix, §2.15.

2.5.5 Carnot engine at maximum power output

While the Carnot engine described above in §2.5.4 has maximum efficiency, it is practically useless, because the isothermal processes must take place infinitely slowly in order for the working material to

remain in thermal equilibrium with each reservoir. Thus, while the work done per cycle is finite, the cycle period is infinite, and the engine *power* is zero.

A modification of the ideal Carnot cycle is necessary to create a practical engine. The idea[13] is as follows. During the isothermal expansion stage, the working material is maintained at a temperature $T_{2\rm w} < T_2$. The temperature difference between the working material and the hot reservoir drives a thermal current,

$$\frac{đQ_2}{dt} = \kappa_2 \, (T_2 - T_{2\rm w}) \quad . \tag{2.82}$$

Here, κ_2 is a *transport coefficient* which describes the *thermal conductivity* of the chamber walls, multiplied by a geometric parameter (which is the ratio of the total wall area to its thickness). Similarly, during the isothermal compression, the working material is maintained at a temperature $T_{1\rm w} > T_1$, which drives a thermal current to the cold reservoir,

$$\frac{đ\mathcal{Q}_1}{dt} = \kappa_1 \, (T_{1\rm w} - T_1) \quad . \tag{2.83}$$

Now let us assume that the upper isothermal stage requires a duration Δt_2 and the lower isotherm a duration Δt_1. Then

$$Q_2 = \kappa_2 \, \Delta t_2 \, (T_2 - T_{2\rm w}) \tag{2.84}$$

$$\mathcal{Q}_1 = \kappa_1 \, \Delta t_1 \, (T_{1\rm w} - T_1) \quad . \tag{2.85}$$

Assuming that the working fluid undergoes an internally reversible cycle, even though heat transfer between the working fluid and the reservoirs is irreversible, we have

$$\frac{\mathcal{Q}_1}{T_{1\rm w}} = \frac{Q_2}{T_{2\rm w}} \quad , \tag{2.86}$$

which says

$$\frac{\Delta t_1}{\Delta t_2} = \frac{\kappa_2 \, T_{1\rm w} \, (T_2 - T_{2\rm w})}{\kappa_1 \, T_{2\rm w} \, (T_{1\rm w} - T_1)} \quad . \tag{2.87}$$

The power is

$$P = \frac{Q_2 - \mathcal{Q}_1}{(1+\alpha) \, (\Delta t_1 + \Delta t_2)} \quad , \tag{2.88}$$

where we assume that the adiabatic stages require a combined time of $\alpha \, (\Delta t_1 + \Delta t_2)$. Thus, we find

$$P = \frac{\kappa_1 \, \kappa_2}{1+\alpha} \cdot \frac{(T_{2\rm w} - T_{1\rm w}) \, (T_{1\rm w} - T_1) \, (T_2 - T_{2\rm w})}{\kappa_1 \, T_{2\rm w} \, (T_{1\rm w} - T_1) + \kappa_2 \, T_{1\rm w} \, (T_2 - T_{2\rm w})} \quad . \tag{2.89}$$

We optimize the engine by maximizing P with respect to the temperatures $T_{1\rm w}$ and $T_{2\rm w}$. This yields

$$T_{2\rm w} = T_2 - \frac{T_2 - \sqrt{T_1 T_2}}{1 + \sqrt{\kappa_2/\kappa_1}} \tag{2.90}$$

$$T_{1\rm w} = T_1 + \frac{\sqrt{T_1 T_2} - T_1}{1 + \sqrt{\kappa_1/\kappa_2}} \quad . \tag{2.91}$$

[13] See F. L. Curzon and B. Ahlborn, *Am. J. Phys.* **43**, 22 (1975). I am grateful to Professor Asle Sudbø for correcting a typo in one expression and providing a simplified form of another.

Power source	T_1 (°C)	T_2 (°C)	$\eta_{\rm Carnot}$	η (theor.)	η (obs.)
West Thurrock (UK) Coal Fired Steam Plant	~ 25	565	0.641	0.40	0.36
CANDU (Canada) PHW Nuclear Reactor	~ 25	300	0.480	0.28	0.30
Larderello (Italy) Geothermal Steam Plant	~ 80	250	0.323	0.175	0.16

Table 2.2: Observed performances of real heat engines, taken from table 1 from Curzon and Ahlborn (1975).

The efficiency at maximum power is then

$$\eta = \frac{Q_2 - \mathcal{Q}_1}{Q_2} = 1 - \frac{T_{1\rm w}}{T_{2\rm w}} = 1 - \sqrt{\frac{T_1}{T_2}} \quad . \tag{2.92}$$

One also finds at maximum power

$$\frac{\Delta t_2}{\Delta t_1} = \sqrt{\frac{\kappa_1}{\kappa_2}} \quad . \tag{2.93}$$

Finally, the maximized power is

$$P_{\rm max} = \frac{\kappa_1 \kappa_2}{1+\alpha} \left(\frac{\sqrt{T_2} - \sqrt{T_1}}{\sqrt{\kappa_1} + \sqrt{\kappa_2}} \right)^2 \quad . \tag{2.94}$$

Table 2.2, taken from the article of Curzon and Ahlborn (1975), shows how the efficiency of this practical Carnot cycle, given by eqn. 2.92, rather accurately predicts the efficiencies of functioning power plants.

2.6 The Entropy

2.6.1 Entropy and heat

The Second Law guarantees us that an engine operating between two heat baths at temperatures T_1 and T_2 must satisfy

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} \le 0 \quad , \tag{2.95}$$

with the equality holding for reversible processes. This is a restatement of eqn. 2.58, after writing $Q_1 = -\mathcal{Q}_1$ for the heat transferred *to* the engine from reservoir #1. Consider now an arbitrary curve in the $p - V$ plane. We can describe such a curve, to arbitrary accuracy, as a combination of Carnot cycles,

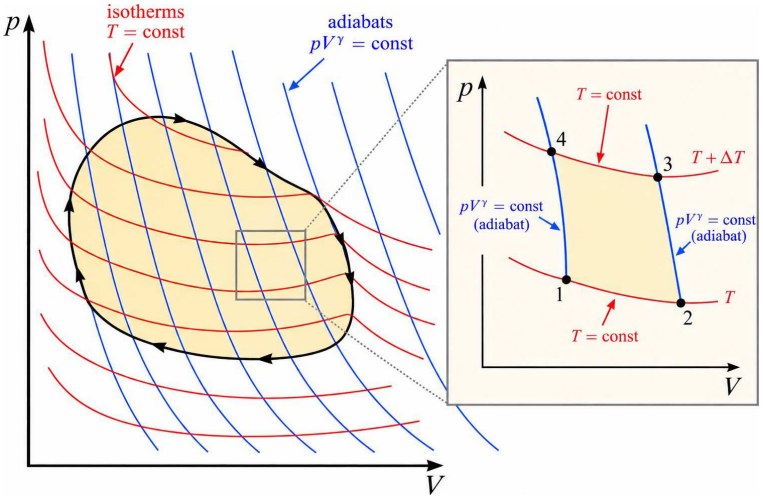


Figure 2.15: An arbitrarily shaped cycle in the $p-V$ plane can be decomposed into a number of smaller Carnot cycles. Red curves indicate isotherms and blue curves adiabats, with $\gamma = \frac{5}{3}$.

as shown in fig. 2.15. Each little Carnot cycle consists of two adiabats and two isotherms. We then conclude

$$\sum_i \frac{Q_i}{T_i} \longrightarrow \oint_{\mathcal{C}} \frac{đQ}{T} \leq 0 \quad , \tag{2.96}$$

with equality holding if all the cycles are reversible. Rudolf Clausius, in 1865, realized that one could then define a new state function, which he called the *entropy*, S, that depended only on the initial and final states of a reversible process:

$$dS = \frac{đQ}{T} \quad \Longrightarrow \quad S_{\rm B} - S_{\rm A} = \int_{\rm A}^{\rm B} \frac{đQ}{T} \quad . \tag{2.97}$$

Since Q is extensive, so is S; the units of entropy are $[S] = \mathrm{J/K}$.

2.6.2 The third law of thermodynamics

Eqn. 2.97 determines the entropy up to a constant. By choosing a standard state Υ, we can define $S_\Upsilon = 0$, and then by taking $\mathrm{A} = \Upsilon$ in the above equation, we can define the absolute entropy S for any state. However, it turns out that this seemingly arbitrary constant S_Υ in the entropy does have consequences, for example in the theory of gaseous equilibrium. The proper definition of entropy, from the point of view of statistical mechanics, will lead us to understand how the zero temperature entropy of a system is related to its quantum mechanical ground state degeneracy. Walther Nernst, in 1906, articulated a principle which is sometimes called the Third Law of Thermodynamics,

The entropy of every system at absolute zero temperature always vanishes.

Again, this is not quite correct, and quantum mechanics tells us that $S(T=0) = k_{\rm B} \log g$, where g is the ground state degeneracy. Nernst's law holds when $g = 1$. A more accurate version of the Third Law:

> *The entropy of a perfect crystal with a unique equilibrium ground state approaches zero as* $T \to 0$.

We can combine the First and Second laws to write

$$dE + đW = đQ \le T\,dS \quad , \tag{2.98}$$

where the equality holds for reversible processes.

2.6.3 Entropy changes in cyclic processes

For a cyclic process, whether reversible or not, the change in entropy around a cycle is zero: $\Delta S_{\rm CYC} = 0$. This is because the entropy S is a state function, with a unique value for every equilibrium state. A cyclical process returns to the same equilibrium state, hence S must return as well to its corresponding value from the previous cycle.

Consider now a general engine, as in fig. 2.12. Let us compute the total entropy change in the entire Universe over one cycle. We have

$$(\Delta S)_{\rm TOTAL} = (\Delta S)_{\rm ENGINE} + (\Delta S)_{\rm HOT} + (\Delta S)_{\rm COLD} \quad , \tag{2.99}$$

written as a sum over entropy changes of the engine itself, the hot reservoir, and the cold reservoir[14]. Clearly $(\Delta S)_{\rm ENGINE} = 0$. The changes in the reservoir entropies are

$$(\Delta S)_{\rm HOT} = \int\limits_{T=T_2} \frac{đQ_{\rm HOT}}{T} = -\frac{Q_2}{T_2} \ < \ 0 \tag{2.100}$$

$$(\Delta S)_{\rm COLD} = \int\limits_{T=T_1} \frac{đQ_{\rm COLD}}{T} = \frac{\mathcal{Q}_1}{T_1} = -\frac{Q_1}{T_1} \ > \ 0 \quad , \tag{2.101}$$

because the hot reservoir loses heat $Q_2 > 0$ to the engine, and the cold reservoir gains heat $\mathcal{Q}_1 = -Q_1 > 0$ from the engine. Therefore,

$$(\Delta S)_{\rm TOTAL} = -\left(\frac{Q_1}{T_1} + \frac{Q_2}{T_2}\right) \ge 0 \quad . \tag{2.102}$$

Thus, for a reversible cycle, the net change in the total entropy of the engine plus reservoirs is zero. For an irreversible cycle, there is an increase in total entropy, due to spontaneous processes.

[14] We neglect any interfacial contributions to the entropy change, which will be small compared with the bulk entropy change in the thermodynamic limit of large system size.

2.6.4 Gibbs-Duhem relation

Consider a function $f(x_1, \ldots, x_n)$ which is *homogeneous of degree* k, meaning

$$f(\lambda x_1, \ldots, \lambda x_n) = \lambda^k f(x_1, \ldots, x_n) \tag{2.103}$$

for all $\boldsymbol{x}$ and λ. Thus, $f(x, y) = x^2 + 2xy$ is homogeneous of degree $k = 2$, $f(x, y, z) = x^{-1} \exp(y/z) + \pi xyz^{-3}$ is homogeneous of degree $k = -1$, *etc.* Now differentiate the above equation with respect to λ and then set $\lambda = 1$, in which case we obtain

$$\sum_{i=1}^{n} x_i \frac{\partial f}{\partial x_i} = kf \quad , \tag{2.104}$$

a result known as *Euler's theorem for homogeneous functions*. Try it out for yourself on the above examples!

Now recall the general expression eqn. 2.12 for differential work,

$$đW = -\sum_{j=1}^{\mathsf{d}} y_j \, dX_j - \sum_{a=1}^{\mathsf{c}} \mu_a \, dN_a \quad , \tag{2.105}$$

where the $(-y_j, X_j)$ are conjugate pairs of generalized forces and generalized displacements, and (μ_a, N_a) are conjugate pairs of chemical potentials and species numbers. Here each y_j and μ_a is intensive, while each X_j and N_a is extensive. For reversible systems, we can write

$$dE = đQ - đW = T \, dS + \sum_{j=1}^{\mathsf{d}} y_j \, dX_j + \sum_{a=1}^{\mathsf{c}} \mu_a \, dN_a \quad , \tag{2.106}$$

which says that the energy E is a function of the entropy S, the generalized displacements $\{X_j\}$, and the particle numbers $\{N_a\}$:

$$E = E\big(S, \{X_j\}, \{N_a\}\big) \quad . \tag{2.107}$$

Furthermore, we have

$$T = \left(\frac{\partial E}{\partial S}\right)_{\{X_j, N_a\}} \quad , \quad y_j = \left(\frac{\partial E}{\partial X_j}\right)_{S, \{X_{i(\neq j)}, N_a\}} \quad , \quad \mu_a = \left(\frac{\partial E}{\partial N_a}\right)_{S, \{X_j, N_{b(\neq a)}\}} \tag{2.108}$$

Since E and all its arguments are extensive, we have

$$E\big(\lambda S, \{\lambda X_j\}, \{\lambda N_a\}\big) = \lambda E\big(S, \{X_j\}, \{N_a\}\big) \quad , \tag{2.109}$$

which says that the energy is a homogeneous function of all the extensive variables S, $\{X_j\}$, and $\{N_a\}$, of degree $k = 1$. We then conclude that

$$\begin{aligned} E &= S \frac{\partial E}{\partial S} + \sum_{j=1}^{\mathsf{d}} X_j \frac{\partial E}{\partial X_j} + \sum_{a=1}^{\mathsf{c}} N_a \frac{\partial E}{\partial N_a} \\ &= TS + \sum_{j=1}^{\mathsf{d}} y_j \, X_j + \sum_{a=1}^{\mathsf{c}} \mu_a \, N_a \quad . \end{aligned} \tag{2.110}$$

Taking the differential of eqn. 2.110, and then subtracting eqn. 2.106, we obtain

$$S\,dT + \sum_{j=1}^{\mathsf{d}} X_j\,dy_j + \sum_{a=1}^{\mathsf{c}} N_a\,d\mu_a = 0 \quad . \tag{2.111}$$

This is called the *Gibbs-Duhem relation*. It says that there is one equation of state which may be written in terms of all the intensive quantities alone. For example, for a single component (p, V) system, we have $E = TS - pV + \mu N$ and $p = p(T, \mu)$, the latter following from

$$S\,dT - V dp + N\,d\mu = 0 \quad . \tag{2.112}$$

2.6.5 Entropy for an ideal gas

For an ideal gas, we have $E = \frac{1}{2} f N k_{\rm B} T$, and

$$\begin{aligned} dS &= \frac{1}{T}\,dE + \frac{p}{T}\,dV - \frac{\mu}{T}\,dN \\ &= \tfrac{1}{2} f N k_{\rm B}\,\frac{dT}{T} + \frac{p}{T}\,dV + \left(\tfrac{1}{2} f k_{\rm B} - \frac{\mu}{T}\right) dN \quad . \end{aligned} \tag{2.113}$$

Invoking the ideal gas equation of state $pV = N k_{\rm B} T$, we have

$$dS\big|_N = \tfrac{1}{2} f N k_{\rm B}\,d\log T + N k_{\rm B} d\log V \quad . \tag{2.114}$$

Integrating, we obtain

$$S(T, V, N) = \tfrac{1}{2} f N k_{\rm B}\,\log T + N k_{\rm B}\,\log V + \varphi(N) \quad , \tag{2.115}$$

where $\varphi(N)$ is an arbitrary function. Extensivity of S places restrictions on $\varphi(N)$, so that the most general case is

$$\begin{aligned} S(T, V, N) &= \tfrac{1}{2} f N k_{\rm B}\,\log T + N k_{\rm B}\,\log\left(\frac{V}{N}\right) + Na \\ &= \tfrac{1}{2} f N k_{\rm B}\,\log\left(\frac{E}{N}\right) + N k_{\rm B}\,\log\left(\frac{V}{N}\right) + Nb \quad , \end{aligned} \tag{2.116}$$

where a and b are constants, where $b = a - \frac{1}{2} f k_{\rm B} \log(\frac{1}{2} f k_{\rm B})$. When we study statistical mechanics, we will find that for the monatomic ideal gas the entropy is

$$S(T, V, N) = N k_{\rm B}\left[\tfrac{5}{2} + \log\left(\frac{V}{N\lambda_T^3}\right)\right] \quad , \tag{2.117}$$

where $\lambda_T = \sqrt{2\pi\hbar^2/m k_{\rm B} T}$ is the *thermal wavelength*, which involves Planck's constant h (with $\hbar = h/2\pi$). Let's now contrast two illustrative cases.

- *Adiabatic free expansion* – Suppose the volume freely expands from $V_{\rm i}$ to $V_{\rm f} = r\,V_{\rm i}$, with $r > 1$. Such an expansion can be effected by a removal of a partition between two chambers that are otherwise thermally insulated (see fig. 2.10). We have already seen how this process entails

$$\Delta E = Q = W = 0 \quad , \tag{2.118}$$

and thus for an ideal gas $T_{\rm f} = T_{\rm i}$. But the entropy changes! According to eqn. 2.116, we have

$$\Delta S = S_{\rm f} - S_{\rm i} = N k_{\rm B} \log r \quad . \tag{2.119}$$

- *Reversible adiabatic expansion* – If the gas expands quasistatically and reversibly, then $S = S(E, V, N)$ holds everywhere along the thermodynamic path. We then have, assuming $dN = 0$,

$$\begin{aligned} 0 = dS &= \tfrac{1}{2} f N k_{\rm B} \frac{dE}{E} + N k_{\rm B} \frac{dV}{V} \\ &= N k_{\rm B}\, d\log\left(V E^{f/2}\right) \quad . \end{aligned} \tag{2.120}$$

Integrating, we find

$$\frac{E}{E_0} = \left(\frac{V_0}{V}\right)^{2/f} \quad . \tag{2.121}$$

Thus,

$$E_{\rm f} = r^{-2/f}\, E_{\rm i} \quad \Longleftrightarrow \quad T_{\rm f} = r^{-2/f}\, T_{\rm i} \quad . \tag{2.122}$$

2.6.6 Example system

Consider a model thermodynamic system for which

$$E(S, V, N) = \frac{a S^3}{N V} \quad , \tag{2.123}$$

where a is a constant. We have

$$dE = T\,dS - p\,dV + \mu\,dN \quad , \tag{2.124}$$

and therefore

$$T = \left(\frac{\partial E}{\partial S}\right)_{V,N} = \frac{3aS^2}{NV} \tag{2.125}$$

$$p = -\left(\frac{\partial E}{\partial V}\right)_{S,N} = \frac{aS^3}{NV^2} \tag{2.126}$$

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{S,V} = -\frac{aS^3}{N^2 V} \quad . \tag{2.127}$$

Choosing any two of these equations, we can eliminate S, which is inconvenient for experimental purposes. This yields three equations of state,

$$\frac{T^3}{p^2} = 27a\,\frac{V}{N} \qquad , \qquad \frac{T^3}{\mu^2} = 27a\,\frac{N}{V} \qquad , \qquad \frac{p}{\mu} = -\frac{N}{V} \quad , \tag{2.128}$$

only two of which are independent.

What about C_V and C_p? To find C_V, we recast eqn. 2.125 as $S = \sqrt{NVT/3a}$. We then have

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_{V,N} = \frac{1}{2}\left(\frac{NVT}{3a}\right)^{1/2} = \frac{N}{18a}\,\frac{T^2}{p} \quad , \tag{2.129}$$

where the last equality on the RHS follows upon invoking the first of the equations of state in eqn. 2.128. To find C_p, we eliminate V from eqns. 2.125 and 2.126, obtaining $T^2/p = 9aS/N$. From this we obtain

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_{p,N} = \frac{2N}{9a}\,\frac{T^2}{p} \quad . \tag{2.130}$$

Thus, $C_p/C_V = 4$.

We can derive still more. To find the isothermal compressibility $\kappa_T = -V^{-1}(\partial V/\partial p)_{T,N}$, use the first of the equations of state in eqn. 2.128. To derive the adiabatic compressibility $\kappa_S = -V^{-1}(\partial V/\partial p)_{S,N}$, use eqn. 2.126, and then eliminate the inconvenient variable S.

Suppose we use this system as the working substance for a Carnot engine. Let's compute the work done and the engine efficiency. To do this, it is helpful to eliminate S in the expression for the energy, and to rewrite the equation of state:

$$E = pV = \sqrt{\frac{N}{27a}}\,V^{1/2}\,T^{3/2} \qquad , \qquad p = \sqrt{\frac{N}{27a}}\,\frac{T^{3/2}}{V^{1/2}} \quad . \tag{2.131}$$

We assume $dN = 0$ throughout. We now see that for isotherms,

$$dT = 0 \;:\; \frac{E}{\sqrt{V}} = \text{constant} \tag{2.132}$$

Furthermore, since

$$đW\big|_T = \sqrt{\frac{N}{27a}}\,T^{3/2}\,\frac{dV}{V^{1/2}} = 2\,dE\big|_T \quad , \tag{2.133}$$

we conclude that

$$dT = 0 \;:\; W_{\rm if} = 2(E_{\rm f} - E_{\rm i}) \quad , \quad Q_{\rm if} = E_{\rm f} - E_{\rm i} + W_{\rm if} = 3(E_{\rm f} - E_{\rm i}) \quad . \tag{2.134}$$

For adiabats, eqn. 2.125 says $d(TV) = 0$, and therefore

$$đQ = 0 \;:\; TV = \text{constant} \quad , \quad \frac{E}{T} = \text{constant} \quad , \quad EV = \text{constant} \tag{2.135}$$

as well as $W_{\rm if} = E_{\rm i} - E_{\rm f}$. We can use these relations to derive the following:

$$E_{\rm B} = \sqrt{\frac{V_{\rm B}}{V_{\rm A}}}\,E_{\rm A} \quad , \quad E_{\rm C} = \frac{T_1}{T_2}\sqrt{\frac{V_{\rm B}}{V_{\rm A}}}\,E_{\rm A} \quad , \quad E_{\rm D} = \frac{T_1}{T_2}\,E_{\rm A} \quad . \tag{2.136}$$

Now we can write

$$\begin{aligned} W_{\rm AB} &= 2(E_{\rm B} - E_{\rm A}) = 2\left(\sqrt{\frac{V_{\rm B}}{V_{\rm A}}} - 1\right) E_{\rm A} \\ W_{\rm BC} &= (E_{\rm B} - E_{\rm C}) = \sqrt{\frac{V_{\rm B}}{V_{\rm A}}}\left(1 - \frac{T_1}{T_2}\right) E_{\rm A} \\ W_{\rm CD} &= 2(E_{\rm D} - E_{\rm C}) = \frac{2T_1}{T_2}\left(1 - \sqrt{\frac{V_{\rm B}}{V_{\rm A}}}\right) E_{\rm A} \\ W_{\rm DA} &= (E_{\rm D} - E_{\rm A}) = \left(\frac{T_1}{T_2} - 1\right) E_{\rm A} \end{aligned} \tag{2.137}$$

Adding up all the work, we obtain

$$\begin{aligned} W &= W_{\rm AB} + W_{\rm BC} + W_{\rm CD} + W_{\rm DA} \\ &= 3\left(\sqrt{\frac{V_{\rm B}}{V_{\rm A}}} - 1\right)\left(1 - \frac{T_1}{T_2}\right) E_{\rm A} \quad . \end{aligned} \tag{2.138}$$

Since

$$Q_{\rm AB} = 3(E_{\rm B} - E_{\rm A}) = \tfrac{3}{2} W_{\rm AB} = 3\left(\sqrt{\frac{V_{\rm B}}{V_{\rm A}}} - 1\right) E_{\rm A} \quad , \tag{2.139}$$

we find once again

$$\eta = \frac{W}{Q_{\rm AB}} = 1 - \frac{T_1}{T_2} \quad . \tag{2.140}$$

2.6.7 Measuring the entropy of a substance

If we can measure the heat capacity $C_V(T)$ or $C_p(T)$ of a substance as a function of temperature down to the lowest temperatures, then we can measure the entropy. At constant pressure, for example, we have $T\,dS = C_p\,dT$, hence

$$S(p,T) = S(p,T=0) + \int_0^T dT'\,\frac{C_p(T')}{T'} \quad . \tag{2.141}$$

The zero temperature entropy is $S(p,T=0) = k_{\rm B}\log g$ where g is the quantum ground state degeneracy at pressure p. In cases where $g = 1$ we have $S(p,T=0) = 0$. In some systems, the presence of certain symmetries entails $g > 1$.

2.7 Thermodynamic Potentials

Thermodynamic systems may do work on their environments. Under certain constraints, the work done may be bounded from above by the change in an appropriately defined *thermodynamic potential*.

2.7.1 Energy E

Suppose we wish to create a thermodynamic system from scratch. Let's imagine that we create it from scratch in a thermally insulated box of volume V. The work we must do to assemble the system is then $\mathcal{W} = E$. After we bring all the constituent particles together, pulling them in from infinity (say), the system will have total energy E. After we finish, the system may not be in thermal equilibrium. Spontaneous processes will then occur so as to maximize the system's entropy, but the internal energy remains at E.

We have, from the First Law, $dE = đQ - đW$ and combining this with the Second Law in the form $đQ \le T\,dS$ yields

$$dE \le T\,dS - đW \quad . \tag{2.142}$$

Rearranging terms, we have $đW \le T\,dS - dE$. Hence, *the work done by a thermodynamic system under conditions of constant entropy is bounded above by $-dE$, and the maximum $đW$ is achieved for a reversible process.* It is sometimes useful to define the quantity

$$đW_{\rm free} \equiv đW - p\,dV \quad , \tag{2.143}$$

which is the differential work done by the system other than that required to change its volume. Then we have

$$đW_{\rm free} \le T\,dS - p\,dV - dE \quad , \tag{2.144}$$

and we conclude for systems at fixed (S, V) that $đW_{\rm free} \le -dE$. Recall that in general we have $đW = -\boldsymbol{y} \cdot d\boldsymbol{X} - \boldsymbol{\mu} \cdot d\boldsymbol{N}$, with $\boldsymbol{X} = \{X_1, \ldots, X_{\mathsf{d}}\}$ and $\boldsymbol{N} = \{N_1, \ldots, N_{\mathsf{c}}\}$. For what we may call (p, V) systems, there is only $\mathsf{d} = 1$ force/displacement pair, which is $(y, X) = (-p, V)$.

For single component (p, V) systems in equilibrium, eqn. 2.142 says

$$dE = T\,dS - p\,dV + \mu\,dN \quad . \tag{2.145}$$

Therefore $E = E(S, V, N)$ with

$$T = \left(\frac{\partial E}{\partial S}\right)_{V,N} \quad , \quad -p = \left(\frac{\partial E}{\partial V}\right)_{S,N} \quad , \quad \mu = \left(\frac{\partial E}{\partial N}\right)_{S,V} \quad . \tag{2.146}$$

These expressions are easily generalized to multicomponent systems, magnetic systems, *etc.*

Now consider a single component (p, V) system at fixed (S, V, N). We conclude that $dE \le 0$, which says that spontaneous processes in a system with $dS = dV = dN = 0$ always lead to a reduction in the internal energy E. Therefore, *spontaneous processes drive the internal energy E to a minimum in systems at fixed (S, V, N).*

2.7.2 Helmholtz free energy F

Suppose we spontaneously create our system while it is in constant contact with a thermal reservoir at temperature T. Then as we create our system, it will absorb heat from the reservoir. Therefore, we don't have to supply the full internal energy E, but rather only $E - Q$, since the system receives heat energy

Q from the reservoir. In other words, we must perform work $\mathcal{W} = E - TS$ to create our system, if it is constantly in equilibrium at temperature T. The quantity $E - TS$ is known as the *Helmholtz free energy*, F, which is related to the energy E by a *Legendre transformation*,

$$F = E - TS \quad . \tag{2.147}$$

The general properties of Legendre transformations are discussed in Appendix III, §2.16.

Again invoking the Second Law, we have

$$dF \leq -S\,dT - đW \quad . \tag{2.148}$$

Rearranging terms, we have $đW \leq -S\,dT - dF$, which says that *the work done by a thermodynamic system under conditions of constant temperature is bounded above by $-dF$, and the maximum $đW$ is achieved for a reversible process.* We also have the general result

$$đW_{\rm free} \leq -S\,dT - p\,dV - dF \quad , \tag{2.149}$$

and we conclude, for systems at fixed (T, V), that $đW_{\rm free} \leq -dF$.

Under equilibrium conditions, the equality in eqn. 2.148 holds, and for single component (p, V) systems where $đW = p\,dV - \mu\,dN$ we have $dF = -S\,dT - p\,dV + \mu\,dN$. This says that $F = F(T, V, N)$ with

$$-S = \left(\frac{\partial F}{\partial T}\right)_{V,N} \quad , \quad -p = \left(\frac{\partial F}{\partial V}\right)_{T,N} \quad , \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} \quad . \tag{2.150}$$

For spontaneous processes, $dF \leq -S\,dT - p\,dV + \mu\,dN$ says that *spontaneous processes drive the Helmholtz free energy F to a minimum in systems at fixed (T, V, N).*

2.7.3 Enthalpy H

Suppose that when we spontaneously create our system while it is thermally insulated, but in constant mechanical contact with a 'volume bath' at pressure p. For example, we could create our system inside a thermally insulated chamber with one movable wall where the external pressure is fixed at p. Thus, when creating the system, in addition to the system's internal energy E, we must also perform work pV in order to make room for it. In other words, we must perform work $\mathcal{W} = E + pV$. The quantity $E + pV$ is known as the *enthalpy*, H.[15] The enthalpy is obtained from the energy via a different Legendre transformation than that used to obtain the Helmholtz free energy F, *i.e.*

$$\mathsf{H} = E + pV \quad . \tag{2.151}$$

Again invoking the Second Law, we have

$$d\mathsf{H} \leq T\,dS - đW + p\,dV + V\,dp \quad , \tag{2.152}$$

[15] We use a different font to distinguish enthalpy H from magnetic field H.

hence with $đW_{\rm free} = đW - p\,dV$, we have in general

$$đW_{\rm free} \le T\,dS + V dp - d\mathsf{H} \quad , \tag{2.153}$$

and we conclude, for systems at fixed (S,p), that $đW_{\rm free} \le -d\mathsf{H}$.

In equilibrium, for single component (p,V) systems,

$$d\mathsf{H} = T\,dS + V dp + \mu\,dN \quad , \tag{2.154}$$

which says $\mathsf{H} = \mathsf{H}(S,p,N)$, with

$$T = \left(\frac{\partial \mathsf{H}}{\partial S}\right)_{p,N} \quad , \quad V = \left(\frac{\partial \mathsf{H}}{\partial p}\right)_{S,N} \quad , \quad \mu = \left(\frac{\partial \mathsf{H}}{\partial N}\right)_{S,p} \quad . \tag{2.155}$$

For spontaneous processes, $d\mathsf{H} \le T\,dS + V dp + \mu\,dN$, which says that *spontaneous processes drive the enthalpy H to a minimum in systems at fixed (S,p,N).*

2.7.4 Gibbs free energy G

If we create a thermodynamic system at conditions of constant temperature T and constant pressure p, then it absorbs heat energy $Q = TS$ from the reservoir and we must expend work energy pV in order to make room for it. Thus, the total amount of work we must do in assembling our system is $\mathcal{W} = E - TS + pV$. This is the *Gibbs free energy*, G. The Gibbs free energy is obtained from E after two Legendre transformations, *viz.*

$$G = E - TS + pV \tag{2.156}$$

Note that $G = F + pV = \mathsf{H} - TS$. The Second Law says that

$$dG \le -S\,dT + V dp + p\,dV - đW \quad , \tag{2.157}$$

which we may rearrange as $đW_{\rm free} \le -S\,dT + V dp - dG$. Accordingly, we conclude, for systems at fixed (T,p), that $đW_{\rm free} \le -dG$.

For equilibrium single component (p,V) systems, the differential of G is

$$dG = -S\,dT + V dp + \mu\,dN \quad , \tag{2.158}$$

therefore $G = G(T,p,N)$, with

$$-S = \left(\frac{\partial G}{\partial T}\right)_{p,N} \quad , \quad V = \left(\frac{\partial G}{\partial p}\right)_{T,N} \quad , \quad \mu = \left(\frac{\partial G}{\partial N}\right)_{T,p} \quad . \tag{2.159}$$

Recall that Euler's theorem for single component systems requires $E = TS - pV + \mu N$ which says $G = \mu N$. Thus, the chemical potential μ is the Gibbs free energy per particle. For spontaneous processes, $dG \le -S\,dT + V dp + \mu\,dN$, hence *spontaneous processes drive the Gibbs free energy G to a minimum in systems at fixed (T,p,N).*

2.7.5 Grand potential Ω

The grand potential, sometimes called the Landau free energy, is defined by

$$\Omega = E - TS - \sum_{a=1}^{\mathsf{c}} \mu_a N_a \quad . \tag{2.160}$$

The Second Law then requires

$$d\Omega \le -S\,dT - p\,dV - \sum_{a=1}^{\mathsf{c}} N_a\,d\mu_a - đ\widetilde{W}_{\rm free} \quad , \tag{2.161}$$

where we formally define

$$đ\widetilde{W}_{\rm free} \equiv đW - p\,dV + \sum_{a=1}^{\mathsf{c}} \mu_a\,dN_a \quad . \tag{2.162}$$

We then have $đW_{\rm free} \le -S\,dT - p\,dV - \boldsymbol{N}\cdot d\boldsymbol{\mu} - d\Omega$. We conclude that for systems at fixed $(T, V, \boldsymbol{\mu})$ that $đW_{\rm free} \le -d\Omega$.

Under equilibrium conditions for single component (p, V) systems, we have

$$d\Omega = -S\,dT - p\,dV - N\,d\mu \quad , \tag{2.163}$$

hence

$$-S = \left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu} \quad , \quad -p = \left(\frac{\partial\Omega}{\partial V}\right)_{T,\mu} \quad , \quad -N = \left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V} \quad . \tag{2.164}$$

Again invoking eqn. 2.110, we find $\Omega = -pV$, which says that the pressure is the negative of the grand potential per unit volume. For spontaneous processes, $d\Omega \le -S\,dT - p\,dV - Nd\mu$, hence *spontaneous processes drive the grand potential Ω to a minimum in systems at fixed (T, V, μ).*

2.8 Maxwell Relations

Maxwell relations are conditions equating certain derivatives of state variables which follow from the exactness of the differentials of the various state functions. For a general function $\Phi(u_1, u_2, \ldots, u_n)$, if Φ is of class C^2 or smoother (meaning all its second derivatives exist and are continuous), then

$$\frac{\partial^2\Phi}{\partial u_i\,\partial u_j} = \frac{\partial}{\partial u_i}\left(\frac{\partial\Phi}{\partial u_j}\right) = \frac{\partial}{\partial u_j}\left(\frac{\partial\Phi}{\partial u_i}\right) \quad .$$

Let us write

$$d\Phi = R_1\,du_1 + R_2\,du_2 + \ldots + R_n\,du_n \quad ,$$

with $R_j \equiv \partial\Phi/\partial u_j$, where the derivative is computed holding all u_i for $i \ne j$ constant. Then the equality of the mixed second partial derivatives is equivalent to the conditions

$$\left(\frac{\partial R_i}{\partial u_j}\right)_{u_{k(\ne j)}} = \left(\frac{\partial R_j}{\partial u_i}\right)_{u_{k(\ne i)}} \quad .$$

2.8.1 Relations deriving from $E(S, V, N)$

The energy $E(S, V, N)$ is a state function, with

$$dE = T\,dS - p\,dV + \mu\,dN \quad , \tag{2.165}$$

and therefore

$$T = \left(\frac{\partial E}{\partial S}\right)_{V,N} \qquad , \qquad -p = \left(\frac{\partial E}{\partial V}\right)_{S,N} \qquad , \qquad \mu = \left(\frac{\partial E}{\partial N}\right)_{S,V} \quad . \tag{2.166}$$

Taking the mixed second derivatives, we find

$$\frac{\partial^2 E}{\partial S\,\partial V} = \left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial p}{\partial S}\right)_{V,N} \tag{2.167}$$

$$\frac{\partial^2 E}{\partial S\,\partial N} = \left(\frac{\partial T}{\partial N}\right)_{S,V} = \left(\frac{\partial \mu}{\partial S}\right)_{V,N} \tag{2.168}$$

$$\frac{\partial^2 E}{\partial V\,\partial N} = -\left(\frac{\partial p}{\partial N}\right)_{S,V} = \left(\frac{\partial \mu}{\partial V}\right)_{S,N} \quad . \tag{2.169}$$

2.8.2 Relations deriving from $F(T, V, N)$

The energy $F(T, V, N)$ is a state function, with

$$dF = -S\,dT - p\,dV + \mu\,dN \quad , \tag{2.170}$$

and therefore

$$-S = \left(\frac{\partial F}{\partial T}\right)_{V,N} \qquad , \qquad -p = \left(\frac{\partial F}{\partial V}\right)_{T,N} \qquad , \qquad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} \quad . \tag{2.171}$$

Taking the mixed second derivatives, we find

$$\frac{\partial^2 F}{\partial T\,\partial V} = -\left(\frac{\partial S}{\partial V}\right)_{T,N} = -\left(\frac{\partial p}{\partial T}\right)_{V,N} \tag{2.172}$$

$$\frac{\partial^2 F}{\partial T\,\partial N} = -\left(\frac{\partial S}{\partial N}\right)_{T,V} = \left(\frac{\partial \mu}{\partial T}\right)_{V,N} \tag{2.173}$$

$$\frac{\partial^2 F}{\partial V\,\partial N} = -\left(\frac{\partial p}{\partial N}\right)_{T,V} = \left(\frac{\partial \mu}{\partial V}\right)_{T,N} \quad . \tag{2.174}$$

From Gibbs-Duhem, we know that for a single component system any three intensive quantities are related by an equation of state. Thus from the first of the above equations we may write

$$\left(\frac{\partial (S/N)}{\partial (V/N)}\right)_{T,N} = \left(\frac{\partial \mathsf{s}}{\partial \mathsf{v}}\right)_{T} = \left(\frac{\partial p}{\partial T}\right)_{\mathsf{v}} \quad , \tag{2.175}$$

since $\mathsf{s} = S/N$ may be expressed as a function of T and $\mathsf{v} = V/N$ alone[16]. From the second equation, we have, similarly,

$$-\left(\frac{\partial(S/V)}{\partial(N/V)}\right)_{T,V} = \mathsf{v}\left(\frac{\partial \mathsf{s}}{\partial \mathsf{v}}\right)_T - \mathsf{s} = \left(\frac{\partial \mu}{\partial T}\right)_{\mathsf{v}} \quad . \tag{2.176}$$

2.8.3 Relations deriving from $\mathsf{H}(S, p, N)$

The enthalpy $\mathsf{H}(S, p, N)$ satisfies

$$d\mathsf{H} = T\,dS + V\,dp + \mu\,dN \quad , \tag{2.177}$$

which says $\mathsf{H} = \mathsf{H}(S, p, N)$, with

$$T = \left(\frac{\partial \mathsf{H}}{\partial S}\right)_{p,N} \quad , \quad V = \left(\frac{\partial \mathsf{H}}{\partial p}\right)_{S,N} \quad , \quad \mu = \left(\frac{\partial \mathsf{H}}{\partial N}\right)_{S,p} \quad . \tag{2.178}$$

Taking the mixed second derivatives, we find

$$\frac{\partial^2 \mathsf{H}}{\partial S\,\partial p} = \left(\frac{\partial T}{\partial p}\right)_{S,N} = \left(\frac{\partial V}{\partial S}\right)_{p,N} \tag{2.179}$$

$$\frac{\partial^2 \mathsf{H}}{\partial S\,\partial N} = \left(\frac{\partial T}{\partial N}\right)_{S,p} = \left(\frac{\partial \mu}{\partial S}\right)_{p,N} \tag{2.180}$$

$$\frac{\partial^2 \mathsf{H}}{\partial p\,\partial N} = \left(\frac{\partial V}{\partial N}\right)_{S,p} = \left(\frac{\partial \mu}{\partial p}\right)_{S,N} \quad . \tag{2.181}$$

The first and third of these entail

$$\mathsf{v} - \mathsf{s}\left(\frac{\partial \mathsf{v}}{\partial \mathsf{s}}\right)_p = \left(\frac{\partial \mu}{\partial p}\right)_{\mathsf{s}} \quad , \quad \left(\frac{\partial T}{\partial p}\right)_{\mathsf{s}} = \left(\frac{\partial \mathsf{v}}{\partial \mathsf{s}}\right)_p \quad . \tag{2.182}$$

2.8.4 Relations deriving from $G(T, p, N)$

The Gibbs free energy $G(T, p, N)$ satisfies

$$dG = -S\,dT + V\,dp + \mu\,dN \quad , \tag{2.183}$$

therefore $G = G(T, p, N)$, with

$$-S = \left(\frac{\partial G}{\partial T}\right)_{p,N} \quad , \quad V = \left(\frac{\partial G}{\partial p}\right)_{T,N} \quad , \quad \mu = \left(\frac{\partial G}{\partial N}\right)_{T,p} \quad . \tag{2.184}$$

[16] Recall that $v = N_{\rm A}\mathsf{v}$ is the molar volume and $s = N_{\rm A}\mathsf{s}$ the molar entropy.

Taking the mixed second derivatives, we find

$$\frac{\partial^2 G}{\partial T\,\partial p} = -\left(\frac{\partial S}{\partial p}\right)_{T,N} = \left(\frac{\partial V}{\partial T}\right)_{p,N} \tag{2.185}$$

$$\frac{\partial^2 G}{\partial T\,\partial N} = -\left(\frac{\partial S}{\partial N}\right)_{T,p} = \left(\frac{\partial \mu}{\partial T}\right)_{p,N} \tag{2.186}$$

$$\frac{\partial^2 G}{\partial p\,\partial N} = \left(\frac{\partial V}{\partial N}\right)_{T,p} = \left(\frac{\partial \mu}{\partial p}\right)_{T,N} \quad . \tag{2.187}$$

The second and third of these entail

$$\left(\frac{\partial \mu}{\partial T}\right)_p = -\mathsf{s} \qquad , \qquad \left(\frac{\partial \mu}{\partial p}\right)_T = \mathsf{v} \quad . \tag{2.188}$$

2.8.5 Relations deriving from $\Omega(T, V, \mu)$

The grand potential $\Omega(T, V, \mu)$ satisfies

$$d\Omega = -S\,dT - p\,dV - N\,d\mu \quad , \tag{2.189}$$

hence

$$-S = \left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu} \qquad , \qquad -p = \left(\frac{\partial \Omega}{\partial V}\right)_{T,\mu} \qquad , \qquad -N = \left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V} \quad . \tag{2.190}$$

Taking the mixed second derivatives, we find

$$\frac{\partial^2 \Omega}{\partial T\,\partial V} = -\left(\frac{\partial S}{\partial V}\right)_{T,\mu} = -\left(\frac{\partial p}{\partial T}\right)_{V,\mu} \tag{2.191}$$

$$\frac{\partial^2 \Omega}{\partial T\,\partial \mu} = -\left(\frac{\partial S}{\partial \mu}\right)_{T,V} = -\left(\frac{\partial N}{\partial T}\right)_{V,\mu} \tag{2.192}$$

$$\frac{\partial^2 \Omega}{\partial V\,\partial \mu} = -\left(\frac{\partial p}{\partial \mu}\right)_{T,V} = -\left(\frac{\partial N}{\partial V}\right)_{T,\mu} \quad . \tag{2.193}$$

The first and third of these entail

$$\left(\frac{\partial p}{\partial T}\right)_\mu = \frac{\mathsf{s}}{\mathsf{v}} \qquad , \qquad \left(\frac{\partial p}{\partial \mu}\right)_T = \frac{1}{\mathsf{v}} \quad . \tag{2.194}$$

Relations deriving from $S(E, V, N)$

We can also derive Maxwell relations based on the entropy $S(E, V, N)$ itself. For example, we have

$$dS = \frac{1}{T}\,dE + \frac{p}{T}\,dV - \frac{\mu}{T}\,dN \quad . \tag{2.195}$$

Therefore $S = S(E, V, N)$ and

$$\frac{\partial^2 S}{\partial E\,\partial V} = \left(\frac{\partial(T^{-1})}{\partial V}\right)_{E,N} = \left(\frac{\partial(pT^{-1})}{\partial E}\right)_{V,N} \quad , \tag{2.196}$$

et cetera.

2.8.6 Generalized thermodynamic potentials

We have up until now assumed a generalized force-displacement pair $(y, X) = (-p, V)$. But the above results also generalize to *e.g.* magnetic systems, where $(y, X) = (H, M)$. In general, we have

THIS SPACE AVAILABLE	$dE = T\,dS + y\,dX + \mu\,dN$	(2.197)
$F = E - TS$	$dF = -S\,dT + y\,dX + \mu\,dN$	(2.198)
$\mathsf{H} = E - yX$	$d\mathsf{H} = T\,dS - X\,dy + \mu\,dN$	(2.199)
$G = E - TS - yX$	$dG = -S\,dT - X\,dy + \mu\,dN$	(2.200)
$\Omega = E - TS - \mu N$	$d\Omega = -S\,dT + y\,dX - N\,d\mu$.	(2.201)

Generalizing $(-p, V) \to (y, X)$, we also obtain, *mutatis mutandis*, the following Maxwell relations:

$$\left(\frac{\partial T}{\partial X}\right)_{S,N} = \left(\frac{\partial y}{\partial S}\right)_{X,N} \qquad \left(\frac{\partial T}{\partial N}\right)_{S,X} = \left(\frac{\partial \mu}{\partial S}\right)_{X,N} \qquad \left(\frac{\partial y}{\partial N}\right)_{S,X} = \left(\frac{\partial \mu}{\partial X}\right)_{S,N} \tag{2.202}$$

$$\left(\frac{\partial T}{\partial y}\right)_{S,N} = -\left(\frac{\partial X}{\partial S}\right)_{y,N} \qquad \left(\frac{\partial T}{\partial N}\right)_{S,y} = \left(\frac{\partial \mu}{\partial S}\right)_{y,N} \qquad \left(\frac{\partial X}{\partial N}\right)_{S,y} = -\left(\frac{\partial \mu}{\partial y}\right)_{S,N} \tag{2.203}$$

$$\left(\frac{\partial S}{\partial X}\right)_{T,N} = -\left(\frac{\partial y}{\partial T}\right)_{X,N} \qquad \left(\frac{\partial S}{\partial N}\right)_{T,X} = -\left(\frac{\partial \mu}{\partial T}\right)_{X,N} \qquad \left(\frac{\partial y}{\partial N}\right)_{T,X} = \left(\frac{\partial \mu}{\partial X}\right)_{T,N} \tag{2.204}$$

$$\left(\frac{\partial S}{\partial y}\right)_{T,N} = \left(\frac{\partial X}{\partial T}\right)_{y,N} \qquad \left(\frac{\partial S}{\partial N}\right)_{T,y} = -\left(\frac{\partial \mu}{\partial T}\right)_{y,N} \qquad \left(\frac{\partial X}{\partial N}\right)_{T,y} = -\left(\frac{\partial \mu}{\partial y}\right)_{T,N} \tag{2.205}$$

$$\left(\frac{\partial S}{\partial X}\right)_{T,\mu} = -\left(\frac{\partial y}{\partial T}\right)_{X,\mu} \qquad \left(\frac{\partial S}{\partial \mu}\right)_{T,X} = \left(\frac{\partial N}{\partial T}\right)_{X,\mu} \qquad \left(\frac{\partial y}{\partial \mu}\right)_{T,X} = -\left(\frac{\partial N}{\partial X}\right)_{T,\mu} \quad . \tag{2.206}$$

2.9 Equilibrium and Stability

2.9.1 Equilibrium

Suppose we have two systems, A and B, which are free to exchange energy, volume, and particle number, subject to overall conservation rules

$$E_{\rm A} + E_{\rm B} = E \quad , \quad V_{\rm A} + V_{\rm B} = V \quad , \quad N_{\rm A} + N_{\rm B} = N \quad , \tag{2.207}$$

where E, V, and N are fixed. Now let us compute the change in the total entropy of the combined systems when they are allowed to exchange energy, volume, or particle number. We assume that the entropy is additive, *i.e.*

$$\begin{aligned} dS = &\left[\left(\frac{\partial S_{\rm A}}{\partial E_{\rm A}}\right)_{V_{\rm A},N_{\rm A}} - \left(\frac{\partial S_{\rm B}}{\partial E_{\rm B}}\right)_{V_{\rm B},N_{\rm B}}\right] dE_{\rm A} + \left[\left(\frac{\partial S_{\rm A}}{\partial V_{\rm A}}\right)_{E_{\rm A},N_{\rm A}} - \left(\frac{\partial S_{\rm B}}{\partial V_{\rm B}}\right)_{E_{\rm B},N_{\rm B}}\right] dV_{\rm A} \\ &+ \left[\left(\frac{\partial S_{\rm A}}{\partial N_{\rm A}}\right)_{E_{\rm A},V_{\rm A}} - \left(\frac{\partial S_{\rm B}}{\partial N_{\rm B}}\right)_{E_{\rm B},V_{\rm B}}\right] dN_{\rm A} \quad . \end{aligned} \tag{2.208}$$

Note that we have used $dE_{\rm B} = -dE_{\rm A}$, $dV_{\rm B} = -dV_{\rm A}$, and $dN_{\rm B} = -dN_{\rm A}$. Now we know from the Second Law that spontaneous processes result in $T\,dS > 0$, which means that S tends to a maximum. If S is a maximum, it must be that the coefficients of $dE_{\rm A}$, $dV_{\rm A}$, and $dN_{\rm A}$ all vanish, else we could increase the total entropy of the system by a judicious choice of these three differentials. From $T\,dS = dE + p\,dV - \mu\,dN$, we have

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} \quad , \quad \frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N} \quad , \quad \frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{E,V} \quad . \tag{2.209}$$

Thus, we conclude that in order for the system to be in equilibrium, so that S is maximized and can increase no further under spontaneous processes, we must have

$$T_{\rm A} = T_{\rm B} \qquad \text{(thermal equilibrium)} \tag{2.210}$$

$$\frac{p_{\rm A}}{T_{\rm A}} = \frac{p_{\rm B}}{T_{\rm B}} \qquad \text{(mechanical equilibrium)} \tag{2.211}$$

$$\frac{\mu_{\rm A}}{T_{\rm A}} = \frac{\mu_{\rm B}}{T_{\rm B}} \qquad \text{(chemical equilibrium)} \tag{2.212}$$

In general, with conjugate force and displacement (y, X), where X can be exchanged between subsystems, equilibrium requires $y_{\rm A}/T_{\rm A} = y_{\rm B}/T_{\rm B}$.

2.9.2 Stability

Next, consider a uniform system with energy $E' = 2E$, volume $V' = 2V$, and particle number $N' = 2N$. We wish to check that this system is not unstable with respect to spontaneously becoming inhomogeneous. To that end, we imagine dividing the system in half. Each half would have energy E, volume V, and particle number N. But suppose we divided up these quantities differently, so that the left half had

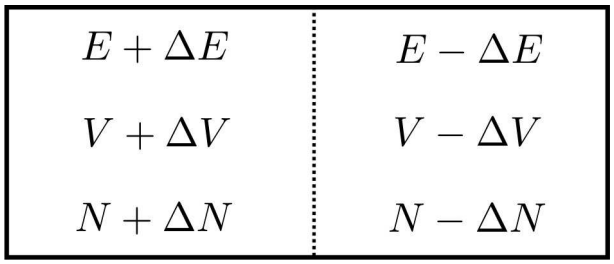


Figure 2.16: To check for an instability, we compare the energy of a system to its total energy when we reapportion its energy, volume, and particle number slightly unequally.

slightly different energy, volume, and particle number than the right, as depicted in fig. 2.16. Does the entropy increase or decrease? We have

$$\begin{aligned}\Delta S &= S(E+\Delta E, V+\Delta V, N+\Delta N) + S(E-\Delta E, V-\Delta V, N-\Delta N) - S(2E, 2V, 2N) \\ &= \frac{\partial^2 S}{\partial E^2}\,(\Delta E)^2 + \frac{\partial^2 S}{\partial V^2}\,(\Delta V)^2 + \frac{\partial^2 S}{\partial N^2}\,(\Delta N)^2 \\ &\qquad + 2\,\frac{\partial^2 S}{\partial E\,\partial V}\,\Delta E\,\Delta V + 2\,\frac{\partial^2 S}{\partial E\,\partial N}\,\Delta E\,\Delta N + 2\,\frac{\partial^2 S}{\partial V\,\partial N}\,\Delta V\,\Delta N \quad .\end{aligned} \tag{2.213}$$

Thus, we can write

$$\Delta S = \sum_{i,j} Q_{ij}\,\Psi_i\,\Psi_j \quad , \tag{2.214}$$

where

$$Q = \begin{pmatrix} \frac{\partial^2 S}{\partial E^2} & \frac{\partial^2 S}{\partial E\,\partial V} & \frac{\partial^2 S}{\partial E\,\partial N} \\ \frac{\partial^2 S}{\partial E\,\partial V} & \frac{\partial^2 S}{\partial V^2} & \frac{\partial^2 S}{\partial V\,\partial N} \\ \frac{\partial^2 S}{\partial E\,\partial N} & \frac{\partial^2 S}{\partial V\,\partial N} & \frac{\partial^2 S}{\partial N^2} \end{pmatrix} \tag{2.215}$$

is the matrix of second derivatives, known in mathematical parlance as the *Hessian*, and $\boldsymbol{\Psi} = (\Delta E, \Delta V, \Delta N)$. Note that Q is a symmetric matrix.

Since S must be a maximum in order for the system to be in equilibrium, we are tempted to conclude that the homogeneous system is stable if and only if all three eigenvalues of Q are negative. If one or more of the eigenvalues is positive, then it is possible to choose a set of variations $\boldsymbol{\Psi}$ such that $\Delta S > 0$, which would contradict the assumption that the homogeneous state is one of maximum entropy. A matrix with this restriction is said to be *negative definite*. While it is true that Q can have no positive eigenvalues, it is clear from homogeneity of $S(E, V, N)$ that one of the three eigenvalues must be zero, corresponding to the eigenvector $\boldsymbol{\Psi} = (E, V, N)$. Homogeneity means $S(\lambda E, \lambda V, \lambda N) = \lambda S(E, V, N)$. Now let us take $\lambda = 1 + \eta$, where η is infinitesimal. Then $\Delta E = \eta E$, $\Delta V = \eta V$, and $\Delta N = \eta N$, and homogeneity says $S(E \pm \Delta E, V \pm \Delta V, N \pm \Delta N) = (1 \pm \eta)\,S(E, V, N)$ and $\Delta S = (1+\eta)S + (1-\eta)S - 2S = 0$. We then have a slightly weaker characterization of Q as *negative semidefinite*.

However, if we fix one of the components of $(\Delta E, \Delta V, \Delta N)$ to be zero, then $\boldsymbol{\Psi}$ must have some component orthogonal to the zero eigenvector, in which case $\Delta S < 0$. Suppose we set $\Delta N = 0$ and we

just examine the stability with respect to inhomogeneities in energy and volume. We then restrict our attention to the upper left 2×2 submatrix of Q. A general symmetric 2×2 matrix may be written

$$Q = \begin{pmatrix} a & b \\ b & c \end{pmatrix} \tag{2.216}$$

It is easy to solve for the eigenvalues of Q. One finds

$$\lambda_\pm = \left(\frac{a+c}{2} \right) \pm \sqrt{\left(\frac{a-c}{2} \right)^2 + b^2} \quad . \tag{2.217}$$

In order for Q to be negative definite, we require $\lambda_+ < 0$ and $\lambda_- < 0$. Thus, $\mathrm{Tr}\, Q = a + c = \lambda_+ + \lambda_- < 0$ and $\det Q = ac - b^2 = \lambda_+ \, \lambda_- > 0$. Taken together, these conditions require

$$a < 0 \qquad , \qquad c < 0 \qquad , \qquad ac > b^2 \quad . \tag{2.218}$$

Going back to thermodynamic variables, this requires

$$\frac{\partial^2 S}{\partial E^2} < 0 \qquad , \qquad \frac{\partial^2 S}{\partial V^2} < 0 \qquad , \qquad \frac{\partial^2 S}{\partial E^2} \cdot \frac{\partial^2 S}{\partial V^2} > \left(\frac{\partial^2 S}{\partial E \, \partial V} \right)^2 \quad . \tag{2.219}$$

Thus *the entropy is a concave function of E and V at fixed N*. Had we set $\Delta E = 0$ and considered the lower right 2×2 block of Q, we'd have concluded that $S(V, N)$ is concave at fixed E. Since $(\partial S/\partial E)_V = T^{-1}$, we have $\partial^2 S/\partial E^2 = -T^{-2}(\partial T/\partial E)_V = -1/T^2 C_V < 0$, whence $C_V > 0$ for stability.

Many thermodynamic systems are held at fixed (T, p, N), which suggests we examine the stability criteria for $G(T, p, N)$. Suppose our system is in equilibrium with a reservoir at temperature T_0 and pressure p_0. Then, suppressing N (which is assumed constant), we have

$$G(T_0, p_0) = E - T_0 \, S + p_0 \, V \quad . \tag{2.220}$$

Now suppose there is a fluctuation in the entropy and the volume of our system, which is held at fixed particle number. Going to second order in ΔS and ΔV, we have

$$\begin{aligned} \Delta G = \left[\left(\frac{\partial E}{\partial S} \right)_V - T_0 \right] \Delta S + \left[\left(\frac{\partial E}{\partial V} \right)_S + p_0 \right] \Delta V \\ + \frac{1}{2} \left[\frac{\partial^2 E}{\partial S^2} \, (\Delta S)^2 + 2 \, \frac{\partial^2 E}{\partial S \, \partial V} \, \Delta S \, \Delta V + \frac{\partial^2 E}{\partial V^2} \, (\Delta V)^2 \right] + \dots \quad . \end{aligned} \tag{2.221}$$

Equilibrium requires that the coefficients of ΔS and ΔV both vanish, *i.e.* that $T = (\partial E/\partial S)_{V,N} = T_0$ and $p = -(\partial E/\partial V)_{S,N} = p_0$. The condition for stability is that $\Delta G > 0$ for all $(\Delta S, \Delta V)$. Stability therefore requires that the Hessian matrix Q be positive definite, with

$$Q = \begin{pmatrix} \frac{\partial^2 E}{\partial S^2} & \frac{\partial^2 E}{\partial S \, \partial V} \\ \\ \frac{\partial^2 E}{\partial S \, \partial V} & \frac{\partial^2 E}{\partial V^2} \end{pmatrix} \quad . \tag{2.222}$$

Thus, we have the following three conditions:

$$\frac{\partial^2 E}{\partial S^2} = \left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V} > 0 \tag{2.223}$$

$$\frac{\partial^2 E}{\partial V^2} = -\left(\frac{\partial p}{\partial V}\right)_S = \frac{1}{V\kappa_S} > 0 \tag{2.224}$$

$$\frac{\partial^2 E}{\partial S^2}\cdot\frac{\partial^2 E}{\partial V^2} - \left(\frac{\partial^2 E}{\partial S\,\partial V}\right)^2 = \frac{T}{V\kappa_S\,C_V} - \left(\frac{\partial T}{\partial V}\right)_S^2 > 0 \quad . \tag{2.225}$$

As we shall discuss below, the quantity $\alpha_S \equiv V^{-1}(\partial V/\partial T)_{S,N}$ is the adiabatic thermal expansivity coefficient. We therefore conclude that stability of any thermodynamic system requires

$$\frac{C_V}{T} > 0 \quad , \quad \kappa_S > 0 \quad , \quad |\alpha_S| > \sqrt{\frac{\kappa_S\,C_V}{VT}} \quad . \tag{2.226}$$

2.10 Applications of Thermodynamics

A discussion of various useful mathematical relations among partial derivatives may be found in the appendix in §2.17. Some facility with the differential multivariable calculus is extremely useful in the analysis of thermodynamics problems.

2.10.1 Adiabatic free expansion revisited

Consider once again the adiabatic free expansion of a gas from initial volume $V_{\rm i}$ to final volume $V_{\rm f} = rV_{\rm i}$. Since the system is not in equilibrium during the free expansion process, the initial and final states do not lie along an adiabat, *i.e.* they do not have the same entropy. Rather, as we found, from $Q = W = 0$, we have that $E_{\rm i} = E_{\rm f}$, which means they have the same *energy*, and, in the case of an ideal gas, the same temperature (assuming N is constant). Thus, the initial and final states lie along an *isotherm*. The situation is depicted in fig. 2.17. Now let us compute the change in entropy $\Delta S = S_{\rm f} - S_{\rm i}$ by integrating along this isotherm. Note that the actual dynamics are *irreversible* and *do not* quasistatically follow any continuous thermodynamic path. However, we can use what is a fictitious thermodynamic path as a means of comparing S in the initial and final states.

We have

$$\Delta S = S_{\rm f} - S_{\rm i} = \int_{V_{\rm i}}^{V_{\rm f}} dV \left(\frac{\partial S}{\partial V}\right)_{T,N} \quad . \tag{2.227}$$

But from a Maxwell equation deriving from F, we have

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial p}{\partial T}\right)_{V,N} \quad , \tag{2.228}$$

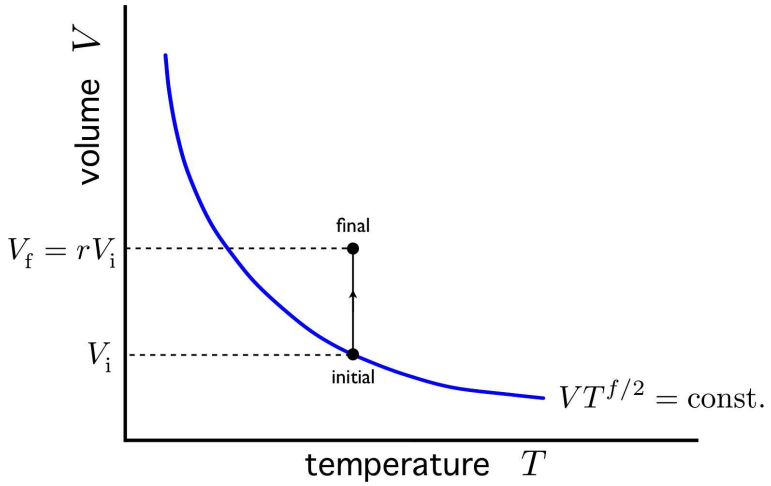


Figure 2.17: Adiabatic free expansion via a thermal path. The initial and final states do not lie along an adiabat! Rather, for an ideal gas, the initial and final states lie along an isotherm.

hence

$$\Delta S = \int_{V_{\rm i}}^{V_{\rm f}} dV \left(\frac{\partial p}{\partial T}\right)_{V,N} \quad . \tag{2.229}$$

For an ideal gas, we can use the equation of state $pV = Nk_{\rm B}T$ to obtain

$$\left(\frac{\partial p}{\partial T}\right)_{V,N} = \frac{Nk_{\rm B}}{V} \quad . \tag{2.230}$$

The integral can now be computed:

$$\Delta S = \int_{V_{\rm i}}^{rV_{\rm i}} dV \, \frac{Nk_{\rm B}}{V} = Nk_{\rm B} \log r \quad , \tag{2.231}$$

as we found before, in eqn. 2.119. What is different about this derivation? Previously, we derived the entropy change from the explicit formula for $S(E, V, N)$. Here, we did not need to know this function. The Maxwell relation allowed us to compute the entropy change using only the equation of state.

2.10.2 Energy and volume

We saw how $E(T, V, N) = \frac{1}{2} f N k_{\rm B} T$ for an ideal gas, independent of the volume. In general we should have

$$E(T, V, N) = N \, \phi\big(T, \tfrac{V}{N}\big) \quad . \tag{2.232}$$

For the ideal gas, $\phi\big(T, V/N\big) = \frac{1}{2} f k_{\rm B} T$ is a function of T alone and is independent on the other intensive quantity V/N. How does energy vary with volume? At fixed temperature and particle number, we

have, from $E = F + TS$,

$$\left(\frac{\partial E}{\partial V}\right)_{T,N} = \left(\frac{\partial F}{\partial V}\right)_{T,N} + T\left(\frac{\partial S}{\partial V}\right)_{T,N} = -p + T\left(\frac{\partial p}{\partial T}\right)_{V,N} \quad , \tag{2.233}$$

where we have used the Maxwell relation $(\partial S/\partial V)_{T,N} = (\partial p/\partial T)_{V,N}$, derived from the mixed second derivative $\partial^2 F/\partial T\,\partial V$. Another way to derive this result is as follows. Write $dE = T\,dS - p\,dV + \mu\,dN$ and then express dS in terms of dT, dV, and dN, resulting in

$$dE = T\left(\frac{\partial S}{\partial T}\right)_{V,N} dT + \left[T\left(\frac{\partial S}{\partial V}\right)_{T,N} - p\right] dV - \left[T\left(\frac{\partial \mu}{\partial T}\right)_{V,N} + \mu\right] dN \quad . \tag{2.234}$$

Now read off $(\partial E/\partial V)_{T,N}$ and use the same Maxwell relation as before to recover eqn. 2.233. Applying this result to the ideal gas law $pV = Nk_{\rm B}T$ results in the vanishing of the RHS, hence for any substance obeying the ideal gas law we must have

$$E(T, V, N) = \nu\,\varepsilon(T) = N\varepsilon(T)/N_{\rm A} \quad . \tag{2.235}$$

2.10.3 van der Waals equation of state

It is clear that the same conclusion follows for any equation of state of the form $p(T, V, N) = T \cdot f(V/N)$, where $f(V/N)$ is an arbitrary function of its argument: the ideal gas law remains valid[17]. This is not true, however, for the van der Waals equation of state,

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \quad , \tag{2.236}$$

where $v = N_{\rm A}V/N$ is the molar volume. We then find (always assuming constant N),

$$\left(\frac{\partial E}{\partial V}\right)_T = \left(\frac{\partial \varepsilon}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p = \frac{a}{v^2} \quad , \tag{2.237}$$

where $E(T, V, N) \equiv \nu\,\varepsilon(T, v)$. We can integrate this to obtain

$$\varepsilon(T, v) = \omega(T) - \frac{a}{v} \quad , \tag{2.238}$$

where $\omega(T)$ is arbitrary. From eqn. 2.31, we immediately have

$$c_V = \left(\frac{\partial \varepsilon}{\partial T}\right)_v = \omega'(T) \quad . \tag{2.239}$$

What about c_p? This requires a bit of work. We start with eqn. 2.32,

$$c_p = \left(\frac{\partial \varepsilon}{\partial T}\right)_p + p\left(\frac{\partial v}{\partial T}\right)_p = c_V + \left(p + \frac{a}{v^2}\right)\left(\frac{\partial v}{\partial T}\right)_p \quad . \tag{2.240}$$

[17] Note $V/N = v/N_{\rm A}$.

gas	$a\ \left(\frac{\mathrm{L}^2\cdot\mathrm{bar}}{\mathrm{mol}^2}\right)$	$b\ \left(\frac{\mathrm{L}}{\mathrm{mol}}\right)$	p_c (bar)	T_c (K)	v_c (L/mol)
Acetone	14.09	0.0994	52.82	505.1	0.2982
Argon	1.363	0.03219	48.72	150.9	0.0966
Carbon dioxide	3.640	0.04267	74.04	304.0	0.1280
Ethanol	12.18	0.08407	63.83	516.3	0.2522
Freon	10.78	0.0998	40.09	384.9	0.2994
Helium	0.03457	0.0237	2.279	5.198	0.0711
Hydrogen	0.2476	0.02661	12.95	33.16	0.0798
Mercury	8.200	0.01696	1055	1723	0.0509
Methane	2.283	0.04278	46.20	190.2	0.1283
Nitrogen	1.408	0.03913	34.06	128.2	0.1174
Oxygen	1.378	0.03183	50.37	154.3	0.0955
Water	5.536	0.03049	220.6	647.0	0.0915

Table 2.3: Van der Waals parameters for some common gases. (*Source: Wikipedia.*)

We may rewrite the equation of state as

$$p = \frac{RT}{v-b} - \frac{a}{v^2} \quad . \tag{2.241}$$

Taking the differential of both sides,

$$\begin{aligned} dp &= \left(\frac{\partial p}{\partial T}\right)_v dT + \left(\frac{\partial p}{\partial v}\right)_T dv \\ &= \frac{R}{v-b}\,dT + \left[-\frac{RT}{(v-b)^2} + \frac{2a}{v^3}\right] dv \quad . \end{aligned} \tag{2.242}$$

Setting $dp = 0$, we may read off

$$\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial p}{\partial T}\right)_v \Bigg/ \left(\frac{\partial p}{\partial v}\right)_T \quad , \tag{2.243}$$

which follows from eqn. 2.487 in the mathematical appendix §2.17 below. Putting this all together, we obtain

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{Rv^3(v-b)}{RTv^3 - 2a(v-b)^2} \quad . \tag{2.244}$$

One immediate result is the following expression for the isobaric thermal expansion coefficient,

$$\alpha_p = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p = \frac{Rv^2(v-b)}{RTv^3 - 2a(v-b)^2} \quad . \tag{2.245}$$

Another result is the difference $c_p - c_V$ from eqn. 2.240,

$$c_p - c_V = \left(p + \frac{a}{v^2}\right)\left(\frac{\partial v}{\partial T}\right)_p = \frac{R^2 T v^3}{RTv^3 - 2a(v-b)^2} \quad . \tag{2.246}$$

To fix $\omega(T)$ and thus $c_V = \omega'(T)$, we consider the $v \to \infty$ limit, where the density of the gas vanishes. In this limit, the gas must be ideal, hence eqn. 2.238 says that $\omega(T) = \frac{1}{2} f RT$. Therefore $c_V(T, v) = \frac{1}{2} f R$, just as in the case of an ideal gas. However, rather than $c_p = c_V + R$, which holds for ideal gases, $c_p(T, v)$ is given by eqn. 2.246, and

$$\begin{aligned} c_V^{\rm VDW} &= \tfrac{1}{2} f R \\ c_p^{\rm VDW} &= \tfrac{1}{2} f R + \frac{R^2 T v^3}{RTv^3 - 2a(v-b)^2} \quad . \end{aligned} \tag{2.247}$$

Note that $c_p(a \to 0) = c_V + R$, which is the ideal gas result.

As we shall see in chapter 7, the van der Waals system is unstable throughout a region of parameters, where it undergoes *phase separation* between high density (liquid) and low density (gas) phases. The above results are valid only in the stable regions of the phase diagram.

2.10.4 General equation of state

Suppose we can't isolate any of the state variables in the equation of state as we did when writing $p = p(T, v)$ above. Rather, let the equation of state take the form $Z(T, p, v) = 0$. Setting consecutively $dv = 0$, $dT = 0$, and $dp = 0$, we then obtain

$$dZ = \left(\frac{\partial Z}{\partial T}\right)_{p,v} dT + \left(\frac{\partial Z}{\partial p}\right)_{T,v} dp + \left(\frac{\partial Z}{\partial v}\right)_{T,p} dv = 0 \quad . \tag{2.248}$$

We then have

$$\begin{aligned} \left(\frac{\partial T}{\partial p}\right)_v &= -\left(\frac{\partial Z}{\partial p}\right)_{T,v} \Big/ \left(\frac{\partial Z}{\partial T}\right)_{p,v} \\ \left(\frac{\partial p}{\partial v}\right)_T &= -\left(\frac{\partial Z}{\partial v}\right)_{T,p} \Big/ \left(\frac{\partial Z}{\partial p}\right)_{T,v} \\ \left(\frac{\partial v}{\partial T}\right)_p &= -\left(\frac{\partial Z}{\partial T}\right)_{p,v} \Big/ \left(\frac{\partial Z}{\partial v}\right)_{T,p} \quad . \end{aligned} \tag{2.249}$$

2.10.5 Thermodynamic response functions

Consider the entropy S expressed as a function of T, V, and N:

$$dS = \left(\frac{\partial S}{\partial T}\right)_{V,N} dT + \left(\frac{\partial S}{\partial V}\right)_{T,N} dV + \left(\frac{\partial S}{\partial N}\right)_{T,V} dN \quad . \tag{2.250}$$

Dividing by dT, multiplying by T, and assuming $dN = 0$ throughout, we have

$$C_p - C_V = T \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_p \quad . \tag{2.251}$$

Appealing to a Maxwell relation derived from $F(T, V, N)$, and then appealing to eqn. 2.486, we have

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V = - \left(\frac{\partial p}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_p . \tag{2.252}$$

This allows us to write

$$C_p - C_V = -T \left(\frac{\partial p}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_p^2 \quad . \tag{2.253}$$

We define the *response functions*,

$$\text{isothermal compressibility:} \quad \kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T = -\frac{1}{V} \frac{\partial^2 G}{\partial p^2} \tag{2.254}$$

$$\text{adiabatic compressibility:} \quad \kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_S = -\frac{1}{V} \frac{\partial^2 H}{\partial p^2} \tag{2.255}$$

$$\text{thermal expansivity:} \quad \alpha_p = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \quad . \tag{2.256}$$

Thus,

$$C_p - C_V = V \frac{T \alpha_p^2}{\kappa_T} \quad , \tag{2.257}$$

or, in terms of intensive quantities,

$$c_p - c_V = \frac{v \, T \alpha_p^2}{\kappa_T} \quad , \tag{2.258}$$

where, as always, $v = V N_{\rm A}/N$ is the molar volume.

This above relation generalizes to any conjugate force-displacement pair $(-p, V) \to (y, X)$:

$$C_y - C_X = -T \left(\frac{\partial y}{\partial T} \right)_X \left(\frac{\partial X}{\partial T} \right)_y = T \left(\frac{\partial y}{\partial X} \right)_T \left(\frac{\partial X}{\partial T} \right)_y^2 \quad . \tag{2.259}$$

For example, we could have $(y, X) = (H^\alpha, M^\alpha)$.

A similar relationship can be derived between the compressibilities κ_T and κ_S. We then clearly must start with the volume, writing

$$dV = \left(\frac{\partial V}{\partial p} \right)_{S,N} dp + \left(\frac{\partial V}{\partial S} \right)_{p,N} dS + \left(\frac{\partial V}{\partial N} \right)_{S,p} dN \quad . \tag{2.260}$$

Dividing by dp, multiplying by $-V^{-1}$, and keeping N constant, we have

$$\kappa_T - \kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial S} \right)_p \left(\frac{\partial S}{\partial p} \right)_T \quad . \tag{2.261}$$

Again we appeal to a Maxwell relation, writing

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \quad , \tag{2.262}$$

and after invoking the chain rule,

$$\left(\frac{\partial V}{\partial S}\right)_p = \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial T}{\partial S}\right)_p = \frac{T}{C_p}\left(\frac{\partial V}{\partial T}\right)_p \quad , \tag{2.263}$$

we obtain

$$\kappa_T - \kappa_S = \frac{v\,T\alpha_p^2}{c_p} \quad . \tag{2.264}$$

Comparing eqns. 2.258 and 2.264, we find

$$(c_p - c_V)\,\kappa_T = (\kappa_T - \kappa_S)\,c_p = v\,T\alpha_p^2 \quad . \tag{2.265}$$

This result entails

$$\frac{c_p}{c_V} = \frac{\kappa_T}{\kappa_S} \quad . \tag{2.266}$$

The corresponding result for magnetic systems is[18]

$$(c_H - c_M)\,\chi_T = (\chi_T - \chi_S)\,c_H = T\left(\frac{\partial m}{\partial T}\right)_H^2 \quad , \tag{2.267}$$

where $m = M/\nu$ is the magnetization per mole of substance, and

$$\text{isothermal susceptibility:} \quad \chi_T = \left(\frac{\partial m}{\partial H}\right)_T = -\frac{1}{\nu}\frac{\partial^2 G}{\partial H^2} \tag{2.268}$$

$$\text{adiabatic susceptibility:} \quad \chi_S = \left(\frac{\partial m}{\partial H}\right)_S = -\frac{1}{\nu}\frac{\partial^2 \mathsf{H}}{\partial H^2} \quad . \tag{2.269}$$

Here the enthalpy and Gibbs free energy are

$$\mathsf{H} = E - HM \qquad d\mathsf{H} = T\,dS - M\,dH \tag{2.270}$$

$$G = E - TS - HM \qquad dG = -S\,dT - M\,dH \quad . \tag{2.271}$$

The previous discussion has assumed an isotropic magnetic system where $\boldsymbol{M}$ and $\boldsymbol{H}$ are collinear, hence $\boldsymbol{H}\cdot\boldsymbol{M} = HM$. In general, we have

$$\chi_T^{\alpha\beta} = \left(\frac{\partial m^\alpha}{\partial H^\beta}\right)_T = -\frac{1}{\nu}\frac{\partial^2 G}{\partial H^\alpha\,\partial H^\beta} \tag{2.272}$$

$$\chi_S^{\alpha\beta} = \left(\frac{\partial m^\alpha}{\partial H^\beta}\right)_S = -\frac{1}{\nu}\frac{\partial^2 H}{\partial H^\alpha\,\partial H^\beta} \quad . \tag{2.273}$$

In this case, the enthalpy and Gibbs free energy are

$$\mathsf{H} = E - \boldsymbol{H}\cdot\boldsymbol{M} \qquad d\mathsf{H} = T\,dS - \boldsymbol{M}\cdot d\boldsymbol{H} \tag{2.274}$$

$$G = E - TS - \boldsymbol{H}\cdot\boldsymbol{M} \qquad dG = -S\,dT - \boldsymbol{M}\cdot d\boldsymbol{H} \quad . \tag{2.275}$$

[18] Recall the subtle font difference in notation: H is enthalpy while H is magnetic field.

2.10.6 Joule effect: free expansion of a gas

Previously we considered the adiabatic free expansion of an ideal gas. We found that $Q = W = 0$ hence $\Delta E = 0$, which means the process is isothermal, since $E = \nu\varepsilon(T)$ is volume-independent. The entropy changes, however, since $S(E, V, N) = Nk_{\rm B}\log(V/N) + \frac{1}{2}fNk_{\rm B}\log(E/N) + Ns_0$. Thus,

$$S_{\rm f} = S_{\rm i} + Nk_{\rm B}\log\left(\frac{V_{\rm f}}{V_{\rm i}}\right) \quad . \tag{2.276}$$

What happens if the gas is nonideal?

We integrate along a fictitious thermodynamic path connecting initial and final states, where $dE = 0$ along the path. We have

$$0 = dE = \left(\frac{\partial E}{\partial V}\right)_T dV + \left(\frac{\partial E}{\partial T}\right)_V dT \tag{2.277}$$

hence

$$\left(\frac{\partial T}{\partial V}\right)_E = -\frac{(\partial E/\partial V)_T}{(\partial E/\partial T)_V} = -\frac{1}{C_V}\left(\frac{\partial E}{\partial V}\right)_T \quad . \tag{2.278}$$

We also have

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p = T\left(\frac{\partial p}{\partial T}\right)_V - p \quad . \tag{2.279}$$

Thus,

$$\left(\frac{\partial T}{\partial V}\right)_E = \frac{1}{C_V}\left[p - T\left(\frac{\partial p}{\partial T}\right)_V\right] \quad . \tag{2.280}$$

Note that the term on the RHS vanishes for any system obeying the ideal gas law. For a nonideal gas,

$$\Delta T = \int_{V_{\rm i}}^{V_{\rm f}} dV \left(\frac{\partial T}{\partial V}\right)_E \quad , \tag{2.281}$$

which is in general nonzero.

Now consider a van der Waals gas, for which

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \quad .$$

We then have

$$p - T\left(\frac{\partial p}{\partial T}\right)_V = -\frac{a}{v^2} = -\frac{a\nu^2}{V^2} \quad . \tag{2.282}$$

In §2.10.3 we concluded that $C_V = \frac{1}{2}f\nu R$ for the van der Waals gas, hence

$$\Delta T = -\frac{2a\nu}{fR}\int_{V_{\rm i}}^{V_{\rm f}} \frac{dV}{V^2} = \frac{2a}{fR}\left(\frac{1}{v_{\rm f}} - \frac{1}{v_{\rm i}}\right) \quad . \tag{2.283}$$

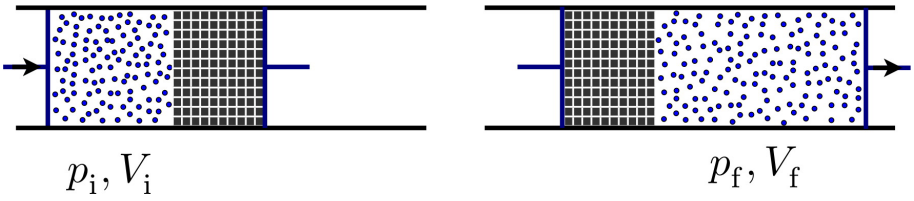


Figure 2.18: In a throttle, a gas is pushed through a porous plug separating regions of different pressure. The change in energy is the work done, hence enthalpy is conserved during the throttling process.

Thus, if $V_{\rm f} > V_{\rm i}$, we have $T_{\rm f} < T_{\rm i}$ and the gas cools upon expansion.

Consider O_2 gas with an initial specific volume of $v_{\rm i} = 22.4\,{\rm L/mol}$, which is the STP value for an ideal gas, freely expanding to a volume $v_{\rm f} = \infty$ for maximum cooling. According to table 2.3, $a = 1.378\,{\rm L}^2\cdot{\rm bar/mol}^2$, and we have $\Delta T = -2a/fRv_i = -0.296\,{\rm K}$, which is a pitifully small amount of cooling. Adiabatic free expansion is a very inefficient way to cool a gas.

2.10.7 Throttling: the Joule-Thomson effect

In a throttle, depicted in fig. 2.18, a gas is forced through a porous plug which separates regions of different pressures. According to the figure, the work done on a given element of gas is

$$W = \int\limits_0^{V_{\rm f}} dV\, p_{\rm f} \;-\; \int\limits_0^{V_{\rm i}} dV\, p_{\rm i} = p_{\rm f}V_{\rm f} - p_{\rm i}V_{\rm i} \quad . \tag{2.284}$$

Now we assume that the system is thermally isolated so that the gas exchanges no heat with its environment, nor with the plug. Then $Q = 0$ so $\Delta E = -W$, and

$$\begin{aligned} E_{\rm i} + p_{\rm i}V_{\rm i} &= E_{\rm f} + p_{\rm f}V_{\rm f} \\ {\rm H}_{\rm i} &= {\rm H}_{\rm f} \quad , \end{aligned} \tag{2.285}$$

where H is enthalpy. Thus, the throttling process is *isenthalpic*. We can therefore study it by defining a fictitious thermodynamic path along which $d{\rm H} = 0$. Then, choosing T and p as state variables,

$$0 = d{\rm H} = \left(\frac{\partial {\rm H}}{\partial T}\right)_p dT \;+\; \left(\frac{\partial {\rm H}}{\partial p}\right)_T dp \tag{2.286}$$

hence

$$\left(\frac{\partial T}{\partial p}\right)_{\rm H} = -\frac{(\partial {\rm H}/\partial p)_T}{(\partial {\rm H}/\partial T)_p} \quad . \tag{2.287}$$

The numerator on the RHS is computed by writing $d{\rm H} = T\,dS + V\,dp$ and then dividing by dp, to obtain

$$\left(\frac{\partial {\rm H}}{\partial p}\right)_T = V + T\left(\frac{\partial S}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p \quad . \tag{2.288}$$

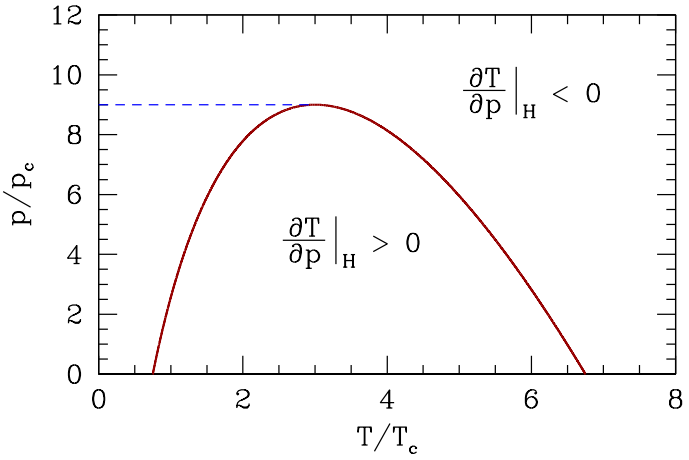


Figure 2.19: Inversion temperature $T^*(p)$ for the van der Waals gas. Pressure and temperature are given in terms of $p_c = a/27b^2$ and $T_c = 8a/27bR$, respectively.

The denominator is

$$\left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial H}{\partial S}\right)_p \left(\frac{\partial S}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p = C_p \quad . \tag{2.289}$$

Thus,

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{1}{c_p}\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right] = \frac{v}{c_p}(T\alpha_p - 1) \quad , \tag{2.290}$$

where $\alpha_p = V^{-1}(\partial V/\partial T)_p$ is the volume expansion coefficient at constant pressure.

From the van der Waals equation of state, we obtain, from eqn. 2.245,

$$T\alpha_p = \frac{T}{v}\left(\frac{\partial v}{\partial T}\right)_p = \frac{RT/v}{p - \frac{a}{v^2} + \frac{2ab}{v^3}} = \frac{v-b}{v - \frac{2a}{RT}\left(\frac{v-b}{v}\right)^2} \quad . \tag{2.291}$$

Assuming $v \gg a/RT$ and $v \gg b$, we have

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{1}{c_p}\left(\frac{2a}{RT} - b\right) \quad . \tag{2.292}$$

Thus, for $T > T^* = 2a/Rb$, we have $(\partial T/\partial p)_H < 0$ and the gas heats up upon an isenthalpic pressure decrease. For $T < T^*$, the gas cools under such conditions.

In fact, there are two inversion temperatures $T^*_{1,2}$ for the van der Waals gas. To see this, we set $T\alpha_p = 1$, which is the criterion for inversion. From eqn. 2.291 it is easy to derive

$$\frac{b}{v} = 1 - \sqrt{\frac{bRT}{2a}} \quad . \tag{2.293}$$

We insert this into the van der Waals equation of state to derive a relationship $T = T^*(p)$ at which $T\alpha_p = 1$ holds. After a little work, we find

$$p = -\frac{3RT}{2b} + \sqrt{\frac{8aRT}{b^3}} - \frac{a}{b^2} \quad . \tag{2.294}$$

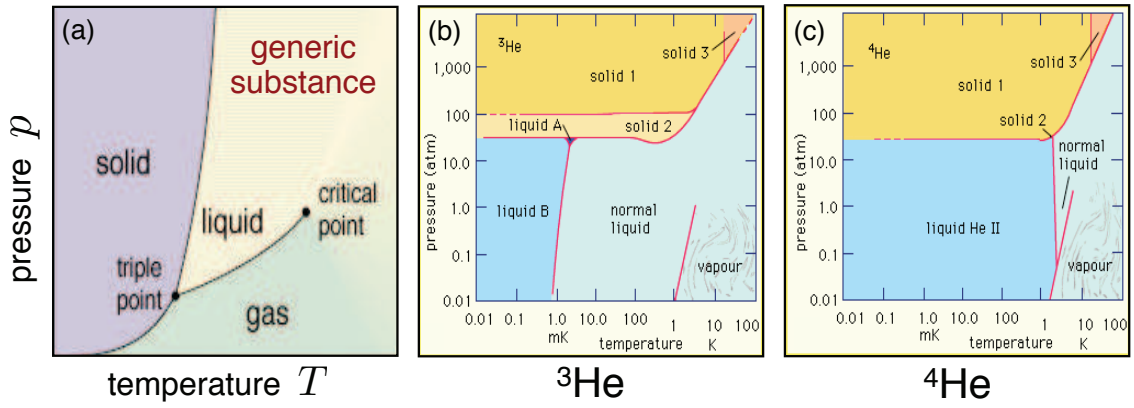


Figure 2.20: (a) Typical thermodynamic phase diagram of a single component p-v-T system, showing triple point (three phase coexistence) and critical point. (*Credit: Univ. of Helsinki.*) Also shown: phase diagrams for ^{3}He (b) and ^{4}He (c). What a difference a neutron makes! (*Credit: Britannica.*)

This is a quadratic equation for $\sqrt{T}$, the solution of which is

$$T^*(p) = \frac{2a}{9\,bR}\left(2 \pm \sqrt{1 - \frac{3b^2 p}{a}}\right)^2 \quad . \tag{2.295}$$

In fig. 2.19 we plot pressure *versus* temperature in scaled units, showing the curve along which the derivative $(\partial T/\partial p)_H = 0$. The volume, pressure, and temperature scales defined are

$$v_{\rm c} = 3b \qquad , \qquad p_{\rm c} = \frac{a}{27\,b^2} \qquad , \qquad T_{\rm c} = \frac{8a}{27\,bR} \quad . \tag{2.296}$$

Values for $p_{\rm c}$, $T_{\rm c}$, and $v_{\rm c}$ are provided in table 2.3. If we define $v = v/v_{\rm c}$, $p = p/p_{\rm c}$, and $T = T/T_{\rm c}$, then the van der Waals equation of state may be written in dimensionless form:

$$\left(p + \frac{3}{v^2}\right)(3v - 1) = 8T \quad . \tag{2.297}$$

In terms of the scaled parameters, the equation for the inversion curve $(\partial T/\partial p)_H = 0$ becomes

$$p = 9 - 36\left(1 - \sqrt{\tfrac{1}{3}T}\,\right)^2 \qquad \Longleftrightarrow \qquad T = 3\Big(1 \pm \tfrac{1}{2}\sqrt{1 - \tfrac{1}{9}\,p}\,\Big)^2 \quad . \tag{2.298}$$

Thus, there is no inversion for $p > 9\,p_{\rm c}$. We are usually interested in the upper inversion temperature, T_2^*, corresponding to the upper sign in eqn. 2.295. The maximum inversion temperature occurs for $p = 0$, where $T^*_{\rm max} = 2a/bR = 27T_{\rm c}/4$. For H_2, from the data in table 2.3, we find $T^*_{\rm max}({\rm H_2}) = 224\,{\rm K}$, which is within 10% of the experimentally measured value of $205\,{\rm K}$.

What happens when H_2 gas leaks from a container with $T > T_2^*$? Since $(\partial T/\partial p)_H < 0$ and $\Delta p < 0$, we have $\Delta T > 0$. The gas warms up, and the heat facilitates the reaction $2\,{\rm H_2} + {\rm O_2} \longrightarrow 2\,{\rm H_2O}$, which releases energy, and we have a nice explosion.

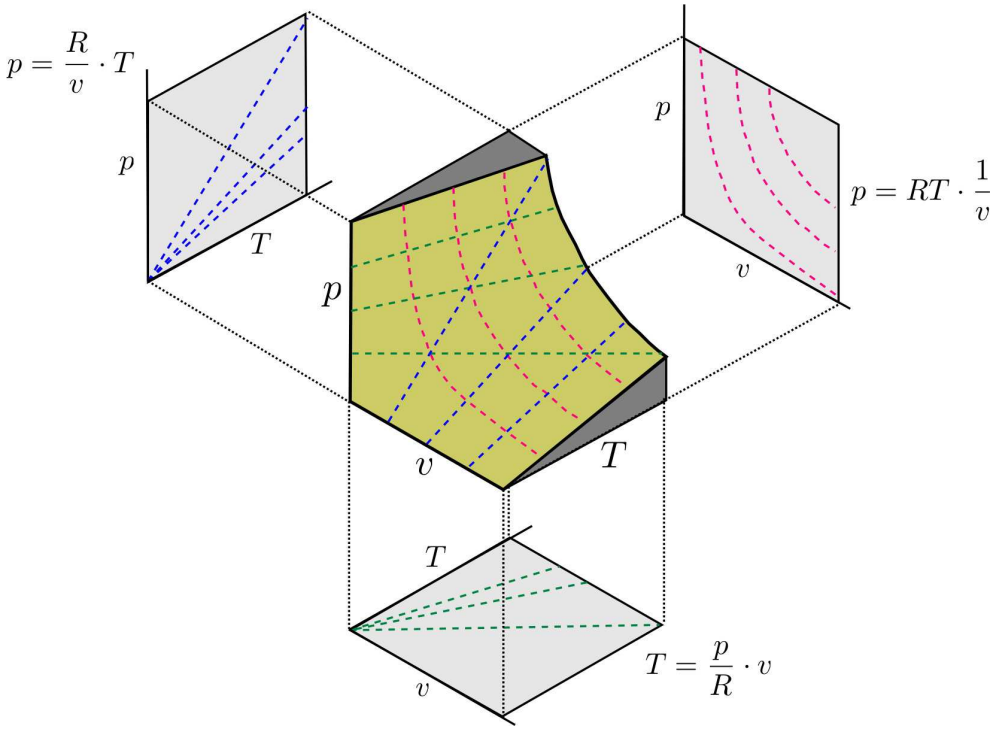


Figure 2.21: The surface $p(v,T) = RT/v$ corresponding to the ideal gas equation of state, and its projections onto the (p,T), (p,v), and (T,v) planes.

2.11 Phase Transitions and Phase Equilibria

A typical phase diagram of a p-v-T system is shown in fig. 2.20(a). The solid lines delineate boundaries between distinct thermodynamic phases. These lines are called *coexistence curves*. Along these curves, we can have coexistence of two phases, and at least one of the thermodynamic potentials is singular. The order of the singularity is often taken as a classification of the phase transition. That is, if one or more of the thermodynamic potentials E, F, G, and H have discontinuous or divergent derivatives of $m^{\rm th}$ and higher, the transition between the respective phases is said to be $m^{\rm th}$ *order*. Modern theories of phase transitions generally recognize only two possibilities: *first order transitions*, where the *order parameter* changes *discontinuously* through the transition, and *continuous transitions* (often called *second order transitions*), where the order parameter vanishes continuously at the boundary from ordered to disordered phases[19]. We'll discuss order parameters when we get to chapter 7.

For a more interesting phase diagram, see fig. 2.20(b,c) for ^{3}He and ^{4}He. The only difference between these two atoms is that the former has one fewer neutron: (2p + 1n + 2e) in ^{3}He *versus* (2p + 2n + 2e) in ^{4}He. As we shall learn when we study quantum statistics, this extra neutron makes all the difference, because ^{3}He is a fermion while ^{4}He is a boson.

[19] Some exotic phase transitions in quantum matter, which do not quite fit the usual classification schemes, have recently been proposed.

2.11.1 p-v-T surfaces

The equation of state for a single component system may be written as

$$f(p, v, T) = 0 \quad . \tag{2.299}$$

This may in principle be inverted to yield $p = p(v, T)$ or $v = v(T, p)$ or $T = T(p, v)$. The single constraint $f(p, v, T)$ on the three state variables defines a *surface* in $\{p, v, T\}$ space. An example of such a surface is shown in fig. 2.21, for the ideal gas.

Real p-v-T surfaces are much richer than that for the ideal gas, because real systems undergo *phase transitions* in which thermodynamic properties are singular or discontinuous along certain curves on the p-v-T surface. An example is shown in fig. 2.22. The high temperature isotherms resemble those of the ideal gas, but as one cools below the *critical temperature* $T_{\rm c}$, the isotherms become singular. Precisely at $T = T_{\rm c}$, the isotherm $p = p(v, T_{\rm c})$ becomes perfectly horizontal at $v = v_{\rm c}$, which is the *critical molar volume*. This means that the isothermal compressibility, $\kappa_T = -v^{-1}(\partial v/\partial p)_T$ *diverges* at $T = T_{\rm c}$. Below $T_{\rm c}$, the isotherms have a flat portion, as shown in fig. 2.25, corresponding to a *two-phase region* where liquid and vapor coexist. In the (p, T) plane, sketched for H_2O in fig. 2.5 and shown for CO_2 in fig. 2.24, this liquid-vapor phase coexistence occurs along a curve, called the vaporization (or boiling) curve. The density changes discontinuously across this curve; for H_2O, the liquid is approximately 1000 times denser than the vapor at atmospheric pressure. The density discontinuity vanishes at the critical point. Note that one can continuously transform between liquid and vapor phases, without encountering any phase transitions, by going around the critical point and avoiding the two-phase region.

In addition to liquid-vapor coexistence, solid-liquid and solid-vapor coexistence also occur, as shown in fig. 2.22. The *triple point* $(\mathrm{T_t}\,,\ p_{\rm t})$ lies at the confluence of these three coexistence regions. For H_2O, the location of the triple point and critical point are given by

$$\mathrm{T_t} = 273.16\,\mathrm{K} \qquad\qquad T_{\rm c} = 647\,\mathrm{K}$$
$$\mathrm{p_t} = 611.7\,\mathrm{Pa} = 6.037 \times 10^{-3}\,\mathrm{atm} \qquad\qquad \mathrm{p_c} = 22.06\,\mathrm{MPa} = 217.7\,\mathrm{atm}$$

2.11.2 The Clausius-Clapeyron relation

Recall that the homogeneity of $E(S, V, N)$ guaranteed $E = TS - pV + \mu N$, from Euler's theorem. It also guarantees a relation between the intensive variables T, p, and μ, according to eqn. 2.112. Let us define $g \equiv G/\nu = N_{\rm A}\mu$, the Gibbs free energy per mole. Then

$$dg = -s\,dT + v\,dp \quad , \tag{2.300}$$

where $s = S/\nu$ and $v = V/\nu$ are the molar entropy and molar volume, respectively. Along a coexistence curve between phase #1 and phase #2, we must have $g_1 = g_2$, since the phases are free to exchange energy and particle number, *i.e.* they are in thermal and chemical equilibrium. This means

$$dg_1 = -s_1\,dT + v_1\,dp = -s_2\,dT + v_2\,dp = dg_2 \quad . \tag{2.301}$$

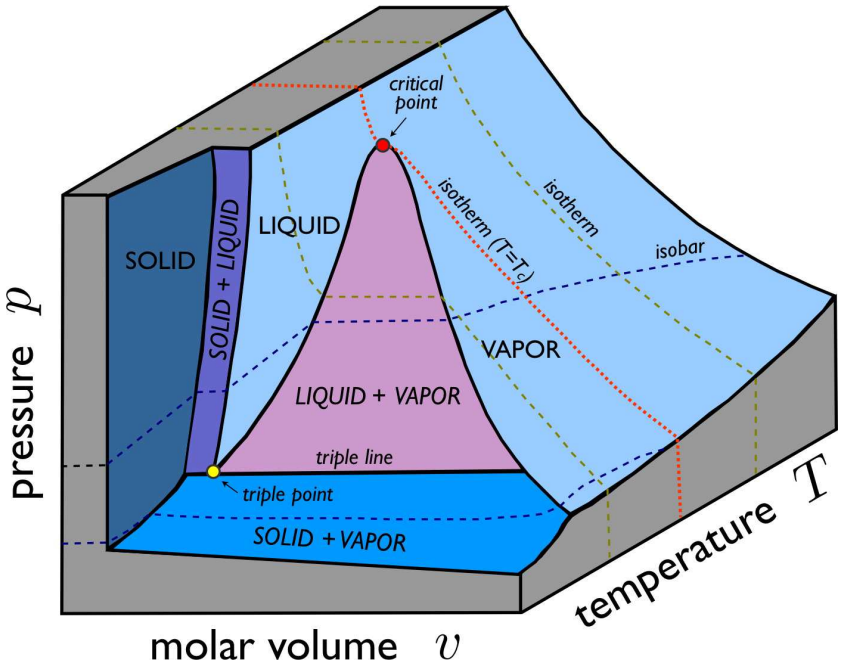


Figure 2.22: A p-v-T surface for a substance which contracts upon freezing. The red dot is the *critical point* and the red dashed line is the *critical isotherm*. The yellow dot is the *triple point* at which there is three phase coexistence of solid, liquid, and vapor.

Therefore, along the coexistence curve we must have

$$\left(\frac{dp}{dT}\right)_{\rm coex} = \frac{s_2 - s_1}{v_2 - v_1} = \frac{\ell}{T\,\Delta v} \quad , \tag{2.302}$$

where $\ell \equiv T\,\Delta s = T\,(s_2 - s_1)$ is the *molar latent heat of transition*. This is known as the *Clapeyron relation*. Heat energy ℓ per mole must be supplied in order to change from phase #1 to phase #2, even without changing p or T. If ℓ is the latent heat per mole, then we write $\tilde{\ell}$ as the latent heat per gram: $\tilde{\ell} = \ell/M$, where M is the molar mass.

Along the liquid-gas coexistence curve, we typically have $v_{\rm gas} \gg v_{\rm liquid}$, and assuming the vapor is ideal, we may write $\Delta v \approx v_{\rm gas} \approx RT/p$, resulting in the *Clausius-Clapeyron relation*,

$$\left(\frac{dp}{dT}\right)_{\rm liq-gas} = \frac{\ell}{T\,\Delta v} \approx \frac{p\,\ell}{RT^2} \quad . \tag{2.303}$$

If ℓ remains constant throughout a section of the liquid-gas coexistence curve, we may integrate the above equation to get

$$\frac{dp}{p} = \frac{\ell}{R}\,\frac{dT}{T^2} \qquad \Rightarrow \qquad p(T) = p(T_0)\,e^{\ell/RT_0}\,e^{-\ell/RT} \quad . \tag{2.304}$$

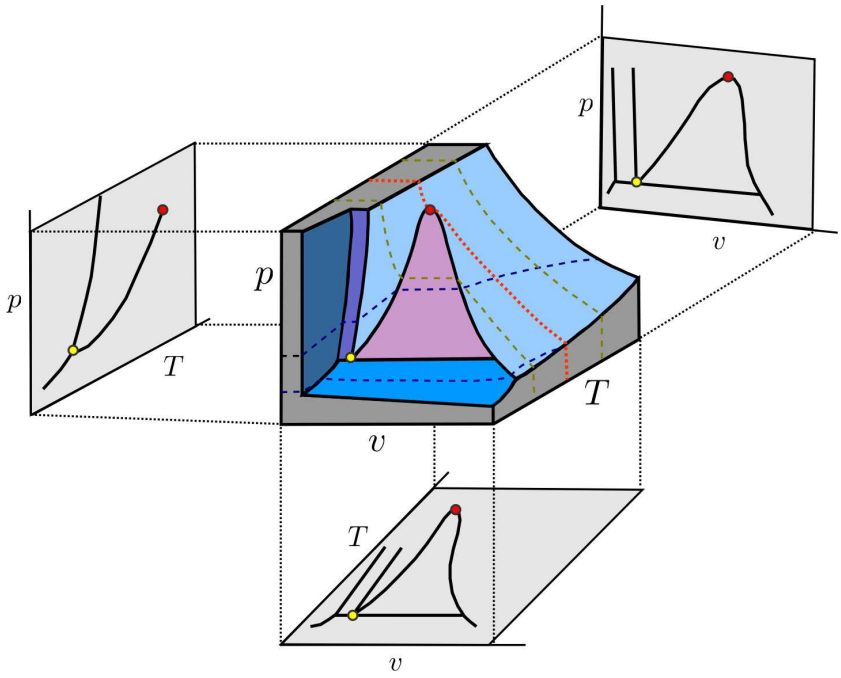


Figure 2.23: Equation of state for a substance which expands upon freezing, projected to the (v, T) and (v, p) and (T, p) planes.

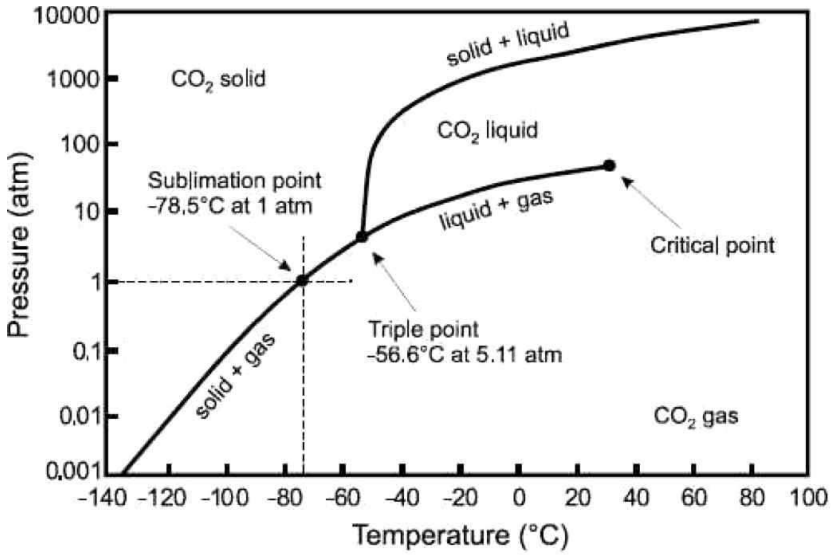


Figure 2.24: Phase diagram for CO_2 in the (p, T) plane. (*Source: www.scifun.org.*)

2.11.3 Liquid-solid line in H_2O

Life on planet earth owes much of its existence to a peculiar property of water: the solid is less dense than the liquid along the coexistence curve[20]. For example at $T = 273.1\,\mathrm{K}$ and $p = 1\,\mathrm{atm}$,

$$\tilde{v}_{\rm water} = 1.00013\,\mathrm{cm}^3/\mathrm{g} \quad , \quad \tilde{v}_{\rm ice} = 1.0907\,\mathrm{cm}^3/\mathrm{g} \quad . \tag{2.305}$$

The latent heat of the transition is $\tilde{\ell} = 333\,\mathrm{J/g} = 79.5\,\mathrm{cal/g}$. Thus,

$$\begin{aligned}\left(\frac{dp}{dT}\right)_{\rm liq-sol} &= \frac{\tilde{\ell}}{T\,\Delta\tilde{v}} = \frac{333\,\mathrm{J/g}}{(273.1\,\mathrm{K})\,(-9.05\times10^{-2}\,\mathrm{cm}^3/\mathrm{g})} \\ &= -1.35\times10^8\,\frac{\mathrm{dyn}}{\mathrm{cm}^2\,\mathrm{K}} = -134\,\frac{\mathrm{atm}}{^\circ\mathrm{C}} \quad .\end{aligned} \tag{2.306}$$

The negative slope of the melting curve is invoked to explain the movement of glaciers: as glaciers slide down a rocky slope, they generate enormous pressure at obstacles[21] Due to this pressure, the story goes, the melting temperature decreases, and the glacier melts around the obstacle, so it can flow past it, after which it refreezes. But it is not the case that the bottom of the glacier melts under the pressure, for consider a glacier of height $h = 1\,\mathrm{km}$. The pressure at the bottom is $p \sim gh/\tilde{v} \sim 10^7\,\mathrm{Pa}$, which is only about 100 atmospheres. Such a pressure can produce only a small shift in the melting temperature of about $\Delta T_{\rm melt} = -0.75^\circ\,\mathrm{C}$.

Does the Clausius-Clapeyron relation explain how we can skate on ice? When my daughter was seven years old, she had a mass of about $M = 20\,\mathrm{kg}$. Her ice skates had blades of width about $5\,\mathrm{mm}$ and length about $10\,\mathrm{cm}$. Thus, even on one foot, she imparted an additional pressure of only

$$\Delta p = \frac{Mg}{A} \approx \frac{20\,\mathrm{kg}\times9.8\,\mathrm{m/s}^2}{(5\times10^{-3}\,\mathrm{m})\times(10^{-1}\,\mathrm{m})} = 3.9\times10^5\,\mathrm{Pa} = 3.9\,\mathrm{atm} \quad . \tag{2.307}$$

The corresponding change in the melting temperature is thus minuscule: $\Delta T_{\rm melt} \approx -0.03^\circ\,\mathrm{C}$.

So why could my daughter skate so nicely? The answer isn't so clear![22] There seem to be two relevant issues in play. First, friction generates heat which can locally melt the surface of the ice. Second, the surface of ice, and of many solids, is naturally slippery. Indeed, this is the case for ice even if one is standing still, generating no frictional forces. Why is this so? It turns out that the Gibbs free energy of the ice-air interface is larger than the sum of free energies of ice-water and water-air interfaces. That is to say, ice, as well as many simple solids, prefers to have a thin layer of liquid on its surface, even at temperatures well below its bulk melting point. If the intermolecular interactions are not short-ranged[23], theory predicts a surface melt thickness $d \propto (T_{\rm m} - T)^{-1/3}$. In fig. 2.26 we show measurements by Gilpin (1980) of the surface melt on ice, down to about $-50^\circ\,\mathrm{C}$. Near $0^\circ\,\mathrm{C}$ the melt layer thickness is about $40\,\mathrm{nm}$,

[20] Were the solid more dense, ponds and lakes would freeze from the bottom, with unfortunate consequences for life on earth.

[21] The melting curve has a negative slope at relatively low pressures, where the solid has the so-called Ih hexagonal crystal structure. At pressures above about 2500 atmospheres, the crystal structure changes, and the slope of the melting curve becomes positive.

[22] For a recent discussion, see R. Rosenberg, *Physics Today* **58**, 50 (2005).

[23] For example, they could be of the van der Waals form, due to virtual dipole fluctuations, with an attractive $1/r^6$ tail.

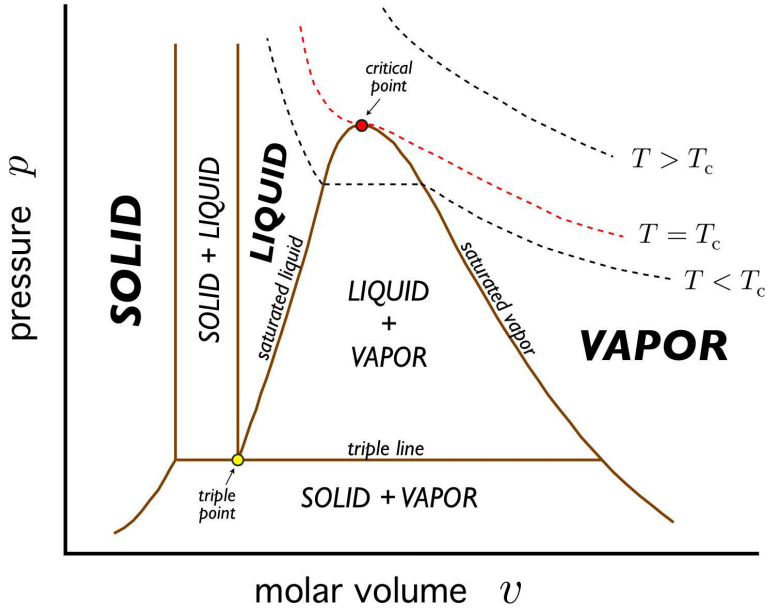


Figure 2.25: Projection of the p-v-T surface of fig. 2.22 onto the (v, p) plane.

but this decreases to $\sim 1\,\text{nm}$ at $T = -35^\circ\,\text{C}$. At very low temperatures, skates stick rather than glide. Of course, the skate material is also important, since that will affect the energetics of the second interface. The 19th century novel, *Hans Brinker, or The Silver Skates* by Mary Mapes Dodge tells the story of the poor but stereotypically decent and hardworking Dutch boy Hans Brinker, who dreams of winning an upcoming ice skating race, along with the top prize: a pair of silver skates. All he has are some lousy wooden skates, which won't do him any good in the race. He has money saved to buy steel skates, but of course his father desperately needs an operation because – I am not making this up – he fell off a dike and lost his mind. The family has no other way to pay for the doctor. What a story! At this point, I imagine the suspense must be too much for you to bear, but this isn't an American Literature class, so you can use Google to find out what happens (or rent the 1958 movie, directed by Sidney Lumet). My point here is that Hans' crappy wooden skates can't compare to the metal ones, even though the surface melt between the ice and the air is the same. The skate blade material also makes a difference, both for the interface energy and, perhaps more importantly, for the generation of friction as well.

2.11.4 Slow melting of ice : a quasistatic but irreversible process

Suppose we have an ice cube initially at temperature $T_0 < \Theta \equiv 273.15\,\text{K}$ (*i.e.* $\Theta = 0^\circ\,\text{C}$) and we toss it into a pond of water. We regard the pond as a heat bath at some temperature $T_1 > \Theta$. Let the mass of the ice be M. How much heat Q is absorbed by the ice in order to raise its temperature to T_1? Clearly

$$Q = M\tilde{c}_{\text{S}}(\Theta - T_0) + M\tilde{\ell} + M\tilde{c}_{\text{L}}(T_1 - \Theta) \quad , \tag{2.308}$$

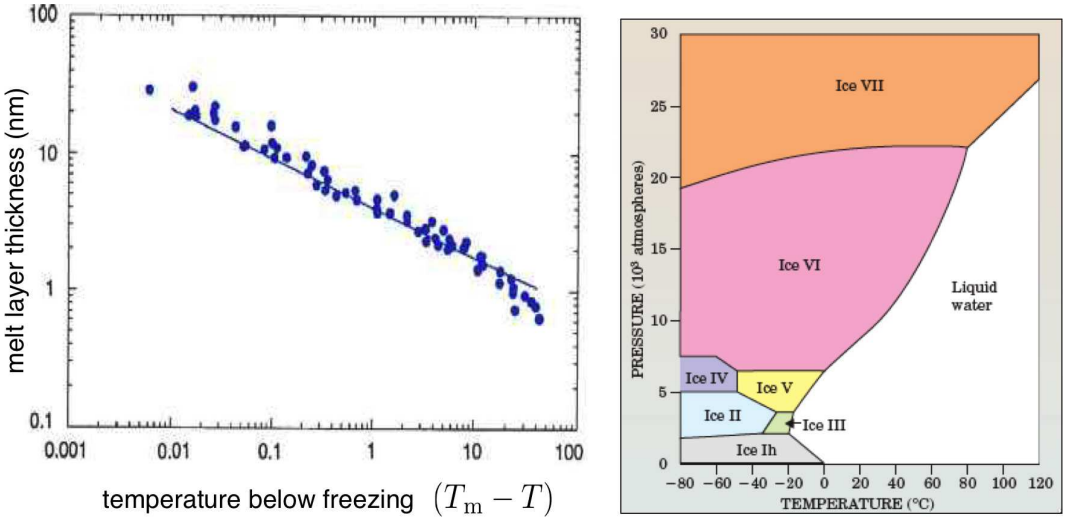


Figure 2.26: Left panel: data from R. R. Gilpin, *J. Colloid Interface Sci.* **77**, 435 (1980) showing measured thickness of the surface melt on ice at temperatures below 0°C. The straight line has slope $-\frac{1}{3}$, as predicted by theory. Right panel: phase diagram of H_2O, showing various high pressure solid phases. (*Source* : *Physics Today*, December 2005).

where $\tilde{c}_{\rm S}$ and $\tilde{c}_{\rm L}$ are the specific heats of ice (solid) and water (liquid), respectively[24], and $\tilde{\ell}$ is the latent heat of melting per unit mass. The pond must give up this much heat to the ice, hence the entropy of the pond, discounting the new water which will come from the melted ice, must decrease:

$$\Delta S_{\rm pond} = -\frac{Q}{T_1} \quad . \tag{2.309}$$

Now we ask what is the entropy change of the H_2O in the ice. We have

$$\begin{aligned} \Delta S_{\rm ice} &= \int \frac{đQ}{T} = \int\limits_{T_0}^{\Theta} dT\, \frac{M\tilde{c}_{\rm S}}{T} + \frac{M\tilde{\ell}}{\Theta} + \int\limits_{\Theta}^{T_1} dT\, \frac{M\tilde{c}_{\rm L}}{T} \\ &= M\tilde{c}_{\rm S} \log\left(\frac{\Theta}{T_0}\right) + \frac{M\tilde{\ell}}{\Theta} + M\tilde{c}_{\rm L} \log\left(\frac{T_1}{\Theta}\right) \quad . \end{aligned} \tag{2.310}$$

The total entropy change of the system is then

$$\begin{aligned} \Delta S_{\rm total} &= \Delta S_{\rm pond} + \Delta S_{\rm ice} \\ &= M\tilde{c}_{\rm S} \log\left(\frac{\Theta}{T_0}\right) - M\tilde{c}_{\rm S}\left(\frac{\Theta - T_0}{T_1}\right) + M\tilde{\ell}\left(\frac{1}{\Theta} - \frac{1}{T_1}\right) + M\tilde{c}_{\rm L} \log\left(\frac{T_1}{\Theta}\right) - M\tilde{c}_{\rm L}\left(\frac{T_1 - \Theta}{T_1}\right) \quad . \end{aligned} \tag{2.311}$$

Now since $T_0 < \Theta < T_1$, we have

$$M\tilde{c}_{\rm S}\left(\frac{\Theta - T_0}{T_1}\right) < M\tilde{c}_{\rm S}\left(\frac{\Theta - T_0}{\Theta}\right) \quad . \tag{2.312}$$

[24]We assume $\tilde{c}_{\rm S}(T)$ and $\tilde{c}_{\rm L}(T)$ have no appreciable temperature dependence, and we regard them both as constants.

Therefore,

$$\Delta S > M\tilde{\ell}\left(\frac{1}{\Theta}-\frac{1}{T_1}\right)+M\tilde{c}_{\rm S}\,f\big(T_0/\Theta\big)+M\tilde{c}_{\rm L}\,f\big(\Theta/T_1\big) \quad , \tag{2.313}$$

where $f(x)=x-1-\log x$. Clearly $f'(x)=1-x^{-1}$ is negative on the interval $(0,1)$, which means that the maximum of $f(x)$ occurs at $x=0$ and the minimum at $x=1$. But $f(0)=\infty$ and $f(1)=0$, which means that $f(x)\geq 0$ for $x\in[0,1]$. Since $T_0<\Theta<T_1$, we conclude $\Delta S_{\rm total}>0$.

Note that by 'slow' we mean that the process is quasistatic and continuous, so that we may use results from equilibrium thermodynamics in our computations. We know that as a practical matter the process is not quasistatic – an ice cube tossed into a pool of water will develop internal temperature variations and will get progressively smaller as it melts from its instantaneous surface. In our idealized example we assume that the temperature is always uniform throughout the ice, which finally begins to melt (*i.e.* change phase) when its temperature throughout reaches Θ. When $T_0=\Theta^-$ and $T_1=\Theta^+$ are infinitesimally below and above the melting temperature, the entropy change in eqn. 2.312 is a positive infinitesimal, and when $T_0=\Theta=T_1$ we have $\Delta S=0$ and the process is reversible.

2.11.5 Generalized Gibbs phase rule

Equilibrium between two phases means that p, T, and $\mu(p,T)$ are identical. From

$$\mu_1(p,T)=\mu_2(p,T) \quad , \tag{2.314}$$

we derive an equation for the slope of the coexistence curve, the Clausius-Clapeyron relation. Note that we have one equation in two unknowns (T,p), so the solution set is a curve. For three phase coexistence, we have

$$\mu_1(p,T)=\mu_2(p,T)=\mu_3(p,T) \quad , \tag{2.315}$$

which gives us two equations in two unknowns. The solution is then a point (or a set of points). A *critical point* also is a solution of two simultaneous equations:

$$\text{critical point} \quad \Longrightarrow \quad v_1(p,T)=v_2(p,T) \quad , \quad \mu_1(p,T)=\mu_2(p,T) \quad . \tag{2.316}$$

Recall $v=N_{\rm A}\big(\frac{\partial\mu}{\partial p}\big)_T$. Note that there can be no four phase coexistence for a simple p-v-T system.

Now for the general result. Suppose we have c species, with particle numbers N_a, where $a=1,\ldots,\mathsf{c}$. It is useful to briefly recapitulate the derivation of the Gibbs-Duhem relation. The internal energy $E(S,V,N_1,\ldots,N_{\mathsf{c}})$ is a homogeneous function of degree one:

$$E(\lambda S,\lambda V,\lambda N_1,\ldots,\lambda N_{\mathsf{c}})=\lambda E(S,V,N_1,\ldots,N_{\mathsf{c}}) \quad . \tag{2.317}$$

From Euler's theorem for homogeneous functions (just differentiate with respect to λ and then set $\lambda=1$), we have

$$E=TS-pV+\sum_{a=1}^{\mathsf{c}}\mu_a N_a \quad . \tag{2.318}$$

Taking the differential, and invoking the First Law,

$$dE=T\,dS-p\,dV+\sum_{a=1}^{\mathsf{c}}\mu_a\,dN_a \quad , \tag{2.319}$$

we arrive at the relation

$$S\,dT - V\,dp + \sum_{a=1}^{\mathsf{c}} N_a\,d\mu_a = 0 \quad , \tag{2.320}$$

of which eqn. 2.111 is a generalization to additional internal 'work' variables. This says that the $\mathsf{c}+2$ quantities $(T, p, \mu_1, \ldots, \mu_{\mathsf{c}})$ are not all independent. We can therefore write

$$\mu_{\mathsf{c}} = \mu_{\mathsf{c}}\big(T, p, \mu_1, \ldots, \mu_{\mathsf{c}-1}\big) \quad . \tag{2.321}$$

If there are φ different phases, then in each phase j, with $j = 1, \ldots, \varphi$, there is a chemical potential $\mu_a^{(j)}$ for each species a. We then have

$$\mu_{\mathsf{c}}^{(j)} = \mu_{\mathsf{c}}^{(j)}\Big(T, p, \mu_1^{(j)}, \ldots, \mu_{\mathsf{c}-1}^{(j)}\Big) \quad . \tag{2.322}$$

Here $\mu_a^{(j)}$ is the chemical potential of the $a^{\rm th}$ species in the $j^{\rm th}$ phase. Thus, there are φ such equations relating the $2 + \mathsf{c}\,\varphi$ variables $\big(T, p, \{\mu_a^{(j)}\}\big)$, meaning that only $2 + (\mathsf{c}-1)\varphi$ of them may be chosen as independent. This, then, is the dimension of 'thermodynamic space' containing a maximal number of intensive variables:

$$d(\mathsf{c}, \varphi) = 2 + \varphi\,(\mathsf{c}-1) \quad . \tag{2.323}$$

To completely specify the state of our system, we of course introduce a single extensive variable, such as the total volume V. Note that the total particle number $N = \sum_{a=1}^{\mathsf{c}} N_a$ may not be conserved in the presence of chemical reactions!

Now suppose we have equilibrium among φ phases. We have implicitly assumed thermal and mechanical equilibrium among all the phases, meaning that p and T are constant. Chemical equilibrium applies on a species-by-species basis. This means

$$\mu_a^{(j)} = \mu_a^{(j')} \tag{2.324}$$

where $j, j' \in \{1, \ldots, \varphi\}$. This gives $\mathsf{c}(\varphi-1)$ independent equations[25]. Thus, we can have *phase equilibrium* among the φ phases of c species over a region of dimension

$$d_{\rm PE}(\mathsf{c}, \varphi) = 2 + \varphi\,(\mathsf{c}-1) - \mathsf{c}\,(\varphi-1) = 2 + \mathsf{c} - \varphi \quad . \tag{2.325}$$

Since $d_{\rm PE} \geq 0$, we must have $\varphi \leq \mathsf{c} + 2$. Thus, with two species ($\mathsf{c} = 2$), we could have at most four phase coexistence.

If the various species can undergo r distinct chemical reactions of the form

$$\zeta_1^{(l)}\,\mathrm{A}_1 + \zeta_2^{(l)}\,\mathrm{A}_2 + \cdots + \zeta_{\mathsf{c}}^{(l)}\,\mathrm{A}_{\mathsf{c}} = 0 \quad , \tag{2.326}$$

where A_a is the chemical formula for species a, and $\zeta_a^{(l)}$ is the stoichiometric coefficient for the $a^{\rm th}$ species in the $l^{\rm th}$ reaction, with $l \in \{1, \ldots, \mathsf{r}\}$, then we have an additional r constraints of the form

$$\sum_{a=1}^{\mathsf{c}} \zeta_a^{(l)}\,\mu_a^{(j)} = 0 \quad . \tag{2.327}$$

[25] Set $j = 1$ and let j' range over the $\varphi - 1$ values $2, \ldots, \varphi$.

Therefore,

$$d_{\rm PE}(\mathsf{c},\varphi,\mathsf{r}) = 2 + \mathsf{c} - \varphi - \mathsf{r} \quad . \tag{2.328}$$

One might ask what value of j are we to use in eqn. 2.327, or do we in fact have φ such equations for each l? The answer is that eqn. 2.324 guarantees that the chemical potential of species a is the same in all the phases, hence it doesn't matter what value one chooses for j in eqn. 2.327.

Let us assume that no reactions take place, *i.e.* $\mathsf{r} = 0$, so the total number of particles $\sum_{a=1}^{\mathsf{c}} N_a$ is conserved. Instead of choosing $(T, p, \mu_1, \ldots, \mu_{\mathsf{c}-1}^{(j)})$ as $d_{\rm TD}$ intensive variables, we could have chosen $(T, p, \mu_1, \ldots, x_{\mathsf{c}-1}^{(j)})$, where $x_a = N_a/N$ is the concentration of species a.

With d independent generalized displacements, the dimensions of the thermodynamic space and regions of phase equilibria are

$$d(\mathsf{c},\varphi) = 1 + \mathsf{d} + \varphi\,(\mathsf{c}-1) \qquad , \qquad d_{\rm PE}(\mathsf{c},\varphi,\mathsf{r}) = 1 + \mathsf{d} + \mathsf{c} - \varphi - \mathsf{r} \quad , \tag{2.329}$$

whence $\varphi \le 1 + \mathsf{d} + \mathsf{c} - \mathsf{r}$.

Why do phase diagrams in the (p, v) and (T, v) plane look different than those in the (p, T) plane?[26] For example, fig. 2.23 shows projections of the p-v-T surface of a typical single component substance onto the (T, v), (p, v), and (p, T) planes. Coexistence takes place along *curves* in the (p, T) plane, but in extended two-dimensional regions in the (T, v) and (p, v) planes. The reason that p and T are special is that temperature, pressure, and chemical potential must be equal throughout an equilibrium phase if it is truly in thermal, mechanical, and chemical equilibrium. This is not the case for an intensive variable such as specific volume $v = N_{\rm A}V/N$ or chemical concentration $x_a = N_a/N$.

2.12 Entropy of Mixing and the Gibbs Paradox

2.12.1 Computing the entropy of mixing

Entropy is widely understood as a measure of disorder. Of course, such a definition should be supplemented by a more precise definition of disorder – after all, one man's trash is another man's treasure. To gain some intuition about entropy, let us explore the mixing of a multicomponent ideal gas with c component species. Let $N = \sum_{a=1}^{c} N_a$ be the total number of particles of all species, and let $x_a = N_a/N$ be the concentration of species a. Note that $\sum_{a=1}^{c} x_a = 1$.

For any substance obeying the ideal gas law $pV = Nk_{\rm B}T$, the entropy is

$$S(T, V, N) = Nk_{\rm B}\log(V/N) + N\phi(T) \quad , \tag{2.330}$$

since $(\partial S/\partial V)_{T,N} = (\partial p/\partial T)_{V,N} = Nk_{\rm B}/V$. Note that in eqn. 2.330 we have divided V by N before taking the logarithm. This is essential if the entropy is to be an extensive function (see §2.6.5). If, as we shall discuss below, the entropy is proportional to the number of ways a system can be 'configured', one

[26] The same can be said for multicomponent systems: the phase diagram in the (T, x) plane at constant p looks different than the phase diagram in the (T, μ) plane at constant p.

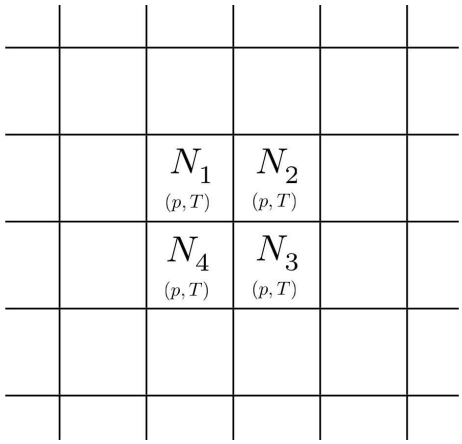


Figure 2.27: A multicomponent system consisting of isolated gases, each at temperature T and pressure p. Then system entropy increases when all the walls between the different subsystems are removed.

might think that the entropy of an ideal gas should scale as $\log(V^N) = N \log V$, since each particle can be anywhere in the volume V. However, if the particles are *indistinguishable*, then permuting the particle labels does not result in a distinct configuration, and so the configurational entropy is proportional to $\log(V^N/N!) \sim N \log(V/N) + N$. The origin of this indistinguishability factor will become clear when we discuss the quantum mechanical formulation of statistical mechanics. For now, note that such a correction is necessary in order that the entropy be an extensive function.

If we did not include this factor and instead wrote $S^*(T, V, N) = Nk_{\rm B} \log V + N\phi(T)$, then we would find $S^*(T, V, N) - 2S^*(T, \frac{1}{2}V, \frac{1}{2}N) = Nk_{\rm B} \log 2$, *i.e.* the total entropy of two identical systems of particles separated by a barrier will increase if the barrier is removed and they are allowed to mix. This seems absurd, though, because we could just as well regard the barriers as invisible. This is known as the *Gibbs paradox*. The resolution of the Gibbs paradox is to include the indistinguishability correction, which renders S extensive, in which case $S(T, V, N) = 2S(T, \frac{1}{2}V, \frac{1}{2}N)$.

Consider now the situation in fig. 2.27, where we have separated the different components into their own volumes V_a. Let the pressure and temperature be the same everywhere, so $pV_a = N_a k_{\rm B} T$. The entropy of the unmixed system is then

$$S_{\rm unmixed} = \sum_a S_a = \sum_a \Big[N_a \, k_{\rm B} \log(V_a/N_a) + N_a \, \phi_a(T) \Big] \quad . \tag{2.331}$$

Now let us imagine removing all the barriers separating the different gases and letting the particles mix thoroughly. The result is that each component gas occupies the full volume V, so the entropy is

$$S_{\rm mixed} = \sum_a S_a = \sum_a \Big[N_a \, k_{\rm B} \log(V/N_a) + N_a \, \phi_a(T) \Big] \quad . \tag{2.332}$$

Thus, the *entropy of mixing* is

$$\begin{aligned} \Delta S_{\rm mix} &= S_{\rm mixed} - S_{\rm unmixed} \\ &= \sum_a N_a \, k_{\rm B} \, \log(V/V_a) = -Nk_{\rm B} \sum_a f_a \log f_a \quad , \end{aligned} \tag{2.333}$$

where $f_a = N_a/N = V_a/V$ is the fraction of species a. Note that $\Delta S_{\rm mix} \geq 0$.

What if all the components were initially identical? It seems absurd that the entropy should increase simply by removing some invisible barriers. This is again the Gibbs paradox. In this case, the resolution of the paradox is to note that the sum in the expression for $S_{\rm mixed}$ is a sum over distinct species. Hence if the particles are all identical, we have $S_{\rm mixed} = Nk_{\rm B}\log(V/N) + N\phi(T) = S_{\rm unmixed}$, hence $\Delta S_{\rm mix} = 0$.

2.12.2 Entropy and combinatorics

As we shall learn when we study statistical mechanics, the entropy may be interpreted in terms of the number of ways $W(E,V,N)$ a system at fixed energy and volume can arrange itself. One has

$$S(E,V,N) = k_{\rm B}\log W(E,V,N) \quad . \tag{2.334}$$

Consider a system consisting of c different species of particles. Initially, each species $a \in \{1,\ldots,\mathsf{c}\}$ is confined to its own region consisting of B_a little boxes, with each little box containing either 0 or 1 of the a-particles. Adding up the total number of boxes over all of the c regions yields $B = \sum_{a=1}^{\mathsf{c}} B_a$ (see fig. 2.28). How many ways W_a are there to configure N_a identical particles among B_a little boxes? Clearly

$$W_a = \binom{B_a}{N_a} = \frac{B_a!}{N_a!\,(B_a - N_a)!} \quad . \tag{2.335}$$

Were the particles distinct, we'd have had $W_a^{\rm distinct} = B_a!/(B_a - N_a)!$, which is $N_a!$ times greater. This is because permuting distinct particles results in a different configuration, and there are $N_a!$ ways to permute N_a particles.

The entropy for species a is then $S_a = k_{\rm B}\log W_a = k_{\rm B}\log\binom{B_a}{N_a}$. We then use Stirling's approximation,

$$\log(K!) = K\log K - K + \tfrac{1}{2}\log K + \tfrac{1}{2}\log(2\pi) + \mathcal{O}(K^{-1}) \quad , \tag{2.336}$$

which is an asymptotic expansion valid for $K \gg 1$. One then finds for $B, N \gg 1$, with $x = N/B \in [0,1]$,

$$\begin{aligned}\log\binom{B}{N} &= \Big(B\log B - B\Big) - \Big(xB\log(xB) - xB\Big) - \Big((1-x)B\log\big((1-x)B\big) - (1-x)B\Big) \\ &= -B\Big[x\log x + (1-x)\log(1-x)\Big] \quad .\end{aligned} \tag{2.337}$$

This is valid up to terms of order B in Stirling's expansion. Since $\log B \ll B$, the next term is small and we are safe to stop here. Summing up the contributions from all the species, we get

$$S_{\rm unmixed} = k_{\rm B}\sum_{a=1}^{\mathsf{c}}\log W_a = -k_{\rm B}\sum_{a=1}^{\mathsf{c}} B_a\Big[x_a\log x_a + (1-x_a)\log(1-x_a)\Big] \quad , \tag{2.338}$$

where $x_a = N_a/B_a$ is the initial dimensionless density of species a.

Now let's remove all the partitions between the different species so that each of the particles is free to explore all of the boxes. The total number of ways of placing N_1 particles of species $a = 1$ through N_{c} particles of species c is

$$W_{\rm mixed} = \frac{B!}{N_0!\,N_1!\cdots N_{\mathsf{c}}!} \quad , \tag{2.339}$$

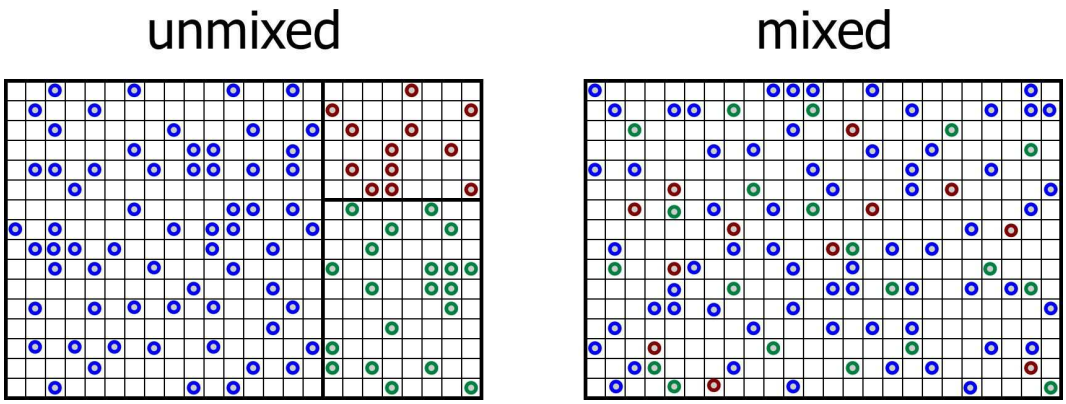


Figure 2.28: Mixing among three different species of particles. The mixed configuration has an additional entropy, $\Delta S_{\rm mix}$.

where $N_0 = B - \sum_{a=1}^{\mathsf{c}} N_a$ is the number of vacant boxes. Again using Stirling's rule, we find

$$S_{\rm mixed} = -k_{\rm B} B \sum_{a=0}^{\mathsf{c}} y_a \log y_a \quad , \tag{2.340}$$

where $y_a = N_a/B$ is the fraction of *all* boxes containing a particle of species a, where we include the $a = 0$ term in the sum to account for the vacant boxes. Note that

$$y_a = \frac{N_a}{B} = \frac{N_a}{B_a} \cdot \frac{B_a}{B} = x_a \, f_a \quad , \tag{2.341}$$

where $f_a \equiv B_a/B$. Note that $\sum_{a=1}^{\mathsf{c}} f_a = 1$ because $B = \sum_{a=1}^{\mathsf{c}} B_a$.

We may now write

$$S_{\rm mixed} = -k_{\rm B} B \sum_{a=1}^{\mathsf{c}} \Big[x_a \, f_a \log(f_a) + f_a \, x_a \log x_a \Big] - k_{\rm B} B \overbrace{\Big(1 - \sum_{a=1}^{\mathsf{c}} x_a \, f_a \Big)}^{y_0} \log\Big(1 - \sum_{a=1}^{\mathsf{c}} x_a f_a \Big) \tag{2.342}$$

If $x_a = x$ for all $a \in \{1, \ldots, \mathsf{c}\}$, meaning that the dimensionless number density is the same in each of the c initial regions, then

$$\begin{aligned} S_{\rm unmixed} &= -k_{\rm B} B \Big[x \log x + (1-x) \log(1-x) \Big] \\ S_{\rm mixed} &= -k_{\rm B} B x \sum_{a=1}^{\mathsf{c}} f_a \log f_a - k_{\rm B} B \Big[x \log x + (1-x) \log(1-x) \Big] \end{aligned} \tag{2.343}$$

and thus, after identifying $N = xB$ is the total number of particles (*i.e.* occupied little boxes), the entropy of mixing is

$$\Delta S_{\rm mix} = -N k_{\rm B} \sum_{a=1}^{\mathsf{c}} f_a \log f_a \quad , \tag{2.344}$$

where $N = \sum_{a=1}^{\mathsf{c}} N_a$ is the total number of particles of all species (excluding vacancies) and $f_a = N_a/N$ is the fraction of particles with species a.

2.12.3 Weak solutions and osmotic pressure

Suppose one of the species is much more plentiful than all the others, and label it with $a = 0$. We will call this the *solvent*. The remaining species are the *solutes*. The entropy of mixing is then

$$\Delta S_{\rm mix} = -k_{\rm B}\left[N_0 \log\left(\frac{N_0}{N_0+\widetilde{N}}\right) + \sum_{a=1}^{\tilde{\mathsf{c}}} N_a \log\left(\frac{N_a}{N_0+\widetilde{N}}\right)\right] \quad , \tag{2.345}$$

where $\widetilde{N} = \sum_{a=1}^{\tilde{\mathsf{c}}} N_a$ is the total number of solute molecules, summed over all solute species. The total number of solute species is defined to be $\tilde{\mathsf{c}}$, with $\mathsf{c} = 1 + \tilde{\mathsf{c}}$ the total number of all species including the solvent. We assume the solution is *weak*, which means $N_a \le \widetilde{N} \ll N_0$. Expanding in powers of $\widetilde{N}/N_0$ and N_a/N_0, we find

$$\Delta S_{\rm mix} = -k_{\rm B}\sum_{a=1}^{\tilde{\mathsf{c}}}\left[N_a \log\left(\frac{N_a}{N_0}\right) - N_a\right] + \frac{k_{\rm B}}{2N_0}\sum_{a,b=1}^{\tilde{\mathsf{c}}} N_a N_b + \mathcal{O}\left(\frac{\widetilde{N}^3}{N_0^2}\right) \quad . \tag{2.346}$$

Consider now a solution consisting of N_0 molecules of a solvent and N_a molecules of species a of solute, where $a = 1, \ldots, \tilde{\mathsf{c}}$, with $\tilde{\mathsf{c}}$ the total number of solute species. Including the solvent, the total number of all species is $\mathsf{c} = 1 + \tilde{\mathsf{c}}$. We begin by expanding the Gibbs free energy $G(T, p, N_0, N_1, \ldots, N_{\tilde{\mathsf{c}}})$ in powers of the solute populations. Recall $G = E - TS + pV$, so we should be careful to include a contribution $\Delta G = -T\Delta S_{\rm mix}$ due to the entropy of mixing. Thus,

$$\begin{aligned} G\big(T, p, N_0, \{N_a\}\big) = N_0\, g_0(T,p) &+ k_{\rm B}T\sum_{a=1}^{\tilde{\mathsf{c}}} N_a \log\left(\frac{N_a}{eN_0}\right) \\ &+ \sum_{a=1}^{\tilde{\mathsf{c}}} N_a\, \omega_a(T,p) + \frac{1}{2N_0}\sum_{a,b=1}^{\tilde{\mathsf{c}}} A_{ab}(T,p)\, N_a\, N_b \quad . \end{aligned} \tag{2.347}$$

The first term on the RHS corresponds to the Gibbs free energy of the solvent. The second term is due to the entropy of mixing. The third term is the contribution to the total free energy from the individual species. Note the factor of e in the denominator inside the logarithm, which accounts for the second term in the brackets on the RHS of eqn. 2.346. The last term is due to interactions between the species plus a contribution from $\Delta S_{\rm mix}$. It is truncated at second order in the solute populations.

The chemical potential for the solvent is

$$\mu_0(T,p) = \frac{\partial G}{\partial N_0} = g_0(T,p) - k_{\rm B}T\sum_{a=1}^{\tilde{\mathsf{c}}} x_a - \tfrac{1}{2}\sum_{a,b=1}^{\tilde{\mathsf{c}}} A_{ab}(T,p)\, x_a\, x_b \quad , \tag{2.348}$$

and the chemical potential for species a is

$$\mu_a(T,p) = \frac{\partial G}{\partial N_a} = k_{\rm B}T\log x_a + \omega_a(T,p) + \sum_{b=1}^{\tilde{\mathsf{c}}} A_{ab}(T,p)\, x_b \quad , \tag{2.349}$$

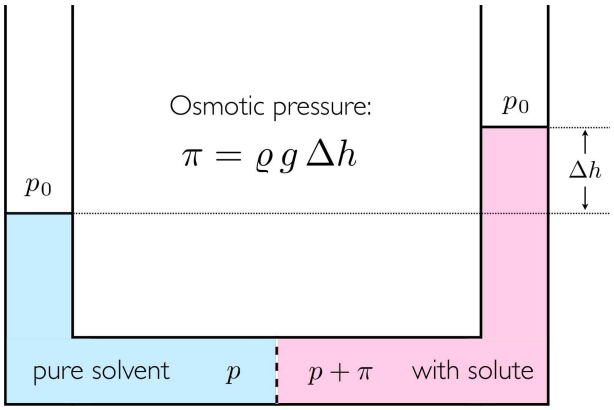


Figure 2.29: Osmotic pressure causes the column on the right side of the U-tube to rise higher than the column on the left by an amount $\Delta h = \pi/\varrho\, g$.

where $x_a = N_a/N_0$ is the concentration of solute species a. By assumption, the last term on the RHS of each of these equations is small, since $\widetilde{N} \ll N_0$, where $\widetilde{N} = \sum_{a=1}^{\tilde{c}} N_a$ is the total number of solute molecules. To lowest order, then, we have

$$\begin{aligned} \mu_0(T,p) &= g_0(T,p) - x\, k_{\rm B} T \\ \mu_a(T,p) &= k_{\rm B} T \log x_a + \omega_a(T,p) \quad , \end{aligned} \tag{2.350}$$

where $x = \sum_{a=1}^{\tilde{c}} x_a$ is the total solute concentration.

If we add sugar to a solution confined by a semipermeable membrane[27], the pressure increases! To see why, consider a situation where a rigid semipermeable membrane separates a solution (solvent plus solutes) from a pure solvent. There is energy exchange through the membrane, so the temperature is T throughout. There is no volume exchange, however: $dV = dV' = 0$, hence the pressure need not be the same. Since the membrane is permeable to the solvent, we have that the chemical potential μ_0 is the same on each side. This means

$$g_0(T, p_{\rm R}) - x k_{\rm B} T = g_0(T, p_{\rm L}) \quad , \tag{2.351}$$

where $p_{\rm L,R}$ is the pressure on the left and right sides of the membrane, and $x = \widetilde{N}/N_0$ is again the total solute concentration. This equation once again tells us that the pressure p cannot be the same on both sides of the membrane. If the pressure difference is small, we can expand in powers of the *osmotic pressure*, $\pi \equiv p_{\rm R} - p_{\rm L}$, and we find

$$\pi = x\, k_{\rm B} T \Big/ \left(\frac{\partial \mu_0}{\partial p}\right)_T \quad . \tag{2.352}$$

But a Maxwell relation (§2.8) guarantees

$$\left(\frac{\partial \mu}{\partial p}\right)_{T,N} = \left(\frac{\partial V}{\partial N}\right)_{T,p} = v(T,p)/N_{\rm A} \quad , \tag{2.353}$$

where $v(T,p)$ is the molar volume of the solvent.

$$\pi v = xRT \quad , \tag{2.354}$$

[27] 'Semipermeable' in this context means permeable to the solvent but not the solute(s).

which looks very much like the ideal gas law, even though we are talking about dense (but 'weak') solutions! The resulting pressure has a demonstrable effect, as sketched in fig. 2.29. Consider a solution containing ν moles of sucrose ($C_{12}H_{22}O_{11}$) per kilogram ($55.52\,\mathrm{mol}$) of water at 30° C. We then find $\pi = 2.5\,\mathrm{atm}$ when $\nu = 0.1$.

One might worry about the expansion in powers of π when π is much larger than the ambient pressure. But in fact the next term in the expansion is smaller than the first term by a factor of $\pi\kappa_T$, where κ_T is the isothermal compressibility. For water one has $\kappa_T \approx 4.4 \times 10^{-5}\,(\mathrm{atm})^{-1}$, hence we can safely ignore the higher order terms in the Taylor expansion.

2.12.4 Effect of impurities on boiling and freezing points

Along the coexistence curve separating liquid and vapor phases, the chemical potentials of the two phases are identical:

$$\mu^0_{\rm L}(T,p) = \mu^0_{\rm V}(T,p) \quad . \tag{2.355}$$

Here we write μ^0 for μ to emphasize that we are talking about a phase with no impurities present. This equation provides a single constraint on the two variables T and p, hence one can, in principle, solve to obtain $T = T^*_0(p)$, which is the equation of the liquid-vapor coexistence curve in the (T,p) plane. Now suppose there is a solute present in the liquid. We then have

$$\mu_{\rm L}(T,p,x) = \mu^0_{\rm L}(T,p) - xk_{\rm B}T \quad , \tag{2.356}$$

where x is the dimensionless solute concentration, summed over all species. The condition for liquid-vapor coexistence now becomes

$$\mu^0_{\rm L}(T,p) - xk_{\rm B}T = \mu^0_{\rm V}(T,p) \quad . \tag{2.357}$$

This will lead to a shift in the boiling temperature at fixed p. Assuming this shift is small, let us expand to lowest order in $\big(T - T^*_0(p)\big)$, writing

$$\mu^0_{\rm L}(T^*_0,p) + \left(\frac{\partial\mu^0_{\rm L}}{\partial T}\right)_p \big(T - T^*_0\big) - xk_{\rm B}T = \mu^0_{\rm V}(T^*_0,p) + \left(\frac{\partial\mu^0_{\rm V}}{\partial T}\right)_p \big(T - T^*_0\big) \quad . \tag{2.358}$$

Note that

$$\left(\frac{\partial\mu}{\partial T}\right)_{p,N} = -\left(\frac{\partial S}{\partial N}\right)_{T,p} \tag{2.359}$$

from a Maxwell relation deriving from exactness of dG. Since S is extensive, we can write $S = (N/N_{\rm A})\,s(T,p)$, where $s(T,p)$ is the molar entropy. Solving for T, we obtain

$$T^*(p,x) = T^*_0(p) + \frac{xR\big[T^*_0(p)\big]^2}{\ell_{\rm v}(p)} \quad , \tag{2.360}$$

where $\ell_{\rm v} = T^*_0 \cdot (s_{\rm V} - s_{\rm L})$ is the *latent heat* of the liquid-vapor transition (see §2.11.2). The shift $\Delta T^* = T^* - T^*_0$ is called the *boiling point elevation*.

Substance	Latent Heat of Fusion $\tilde{\ell}_{\rm f}$ J/g	Melting Point °C	Latent Heat of Vaporization $\tilde{\ell}_{\rm v}$ J/g	Boiling Point °C
C_2H_5OH	108	-114	855	78.3
NH_3	339	-75	1369	-33.34
He	–	–	21	-268.93
H_2	58	-259	455	-253
Pb	24.5	327.5	871	1750
N_2	25.7	-210	200	-196
O_2	13.9	-219	213	-183
H_2O	334	0	2270	100

Table 2.4: Latent heats of fusion and vaporization at $p = 1$ atm.

As an example, consider seawater, which contains approximately $35\,{\rm g}$ of dissolved $\rm Na^+Cl^-$ per kilogram of H_2O. The atomic masses of Na and Cl are 23.0 and 35.4, respectively, hence the total ionic concentration in seawater (neglecting everything but sodium and chlorine) is given by

$$x = \frac{2\cdot 35}{23.0+35.4}\Big/\frac{1000}{18} \approx 0.022 \quad . \tag{2.361}$$

The latent heat of vaporization of H_2O at atmospheric pressure is $\ell = 40.7\,{\rm kJ/mol}$, hence

$$\Delta T^* = \frac{(0.022)(8.3\,{\rm J/mol\,K})(373\,{\rm K})^2}{4.1\times 10^4\,{\rm J/mol}} \approx 0.6\,{\rm K} \quad . \tag{2.362}$$

Put another way, the boiling point elevation of H_2O at atmospheric pressure is about $0.28^\circ{\rm C}$ per percent solute. We can express this as $\Delta T^* = Km$, where the *molality* m is the number of moles of solute per kilogram of solvent. For H_2O, we find $K = 0.51^\circ{\rm C\,kg/mol}$.

Similar considerations apply at the freezing point, when we equate the chemical potential of the solvent plus solute to that of the pure solid. The *latent heat of fusion* for H_2O is about $\ell_{\rm f} = T_{\rm f}^0\cdot(s_{\rm LIQUID} - s_{\rm SOLID}) = 6.01\,{\rm kJ/mol}$[28]. We thus predict a *freezing point depression* of $\Delta T^* = -xR\big[T_0^*\big]^2/\ell_{\rm f} = -1.03^\circ{\rm C}\cdot x[\%]$. This can be expressed once again as $\Delta T^* = -Km$, with $K = 1.86^\circ{\rm C\,kg/mol}$[29].

[28] See table 2.4, and recall $M = 18\,{\rm g}$ is the molar mass of H_2O.

[29] It is more customary to write $\Delta T^* = T^*_{\text{pure solvent}} - T^*_{\text{solution}}$ in the case of the freezing point depression, in which case ΔT^* is positive.

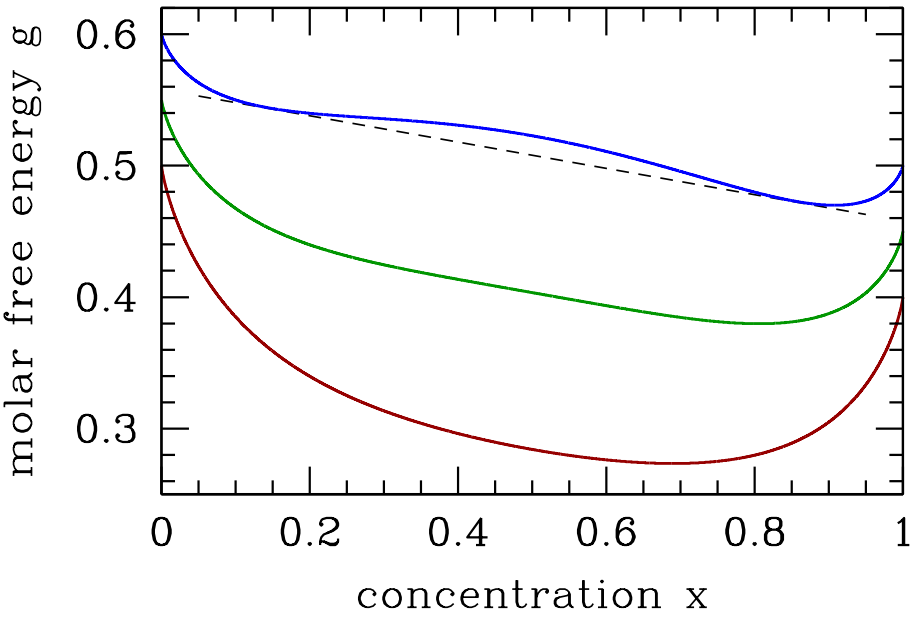


Figure 2.30: Gibbs free energy per particle for a binary solution as a function of concentration $x = x_{\rm B}$ of the B species (pure A at the left end $x = 0$; pure B at the right end $x = 1$), in units of the interaction parameter λ. Dark red curve: $T = 0.65\,\lambda/k_{\rm B} > T_{\rm c}$; green curve: $T = \lambda/2k_{\rm B} = T_{\rm c}$; blue curve: $T = 0.40\,\lambda/k_{\rm B} < T_{\rm c}$. We have chosen $\mu^0_{\rm A} = 0.60\,\lambda - 0.50\,k_{\rm B}T$ and $\mu^0_{\rm B} = 0.50\,\lambda - 0.\,50\,k_{\rm B}T$. Note that the free energy $g(T, p, x)$ is not convex in x for $T < T_{\rm c}$, indicating an instability and necessitating a Maxwell construction.

2.12.5 Binary solutions

Consider a binary solution, and write the Gibbs free energy $G(T, p, N_{\rm A}, N_{\rm B})$ as

$$G(T,p,N_{\rm A},N_{\rm B}) = N_{\rm A}\,\mu^0_{\rm A}(T,p) + N_{\rm B}\,\mu^0_{\rm B}(T,p) + N_{\rm A}k_{\rm B}T\,\log\left(\frac{N_{\rm A}}{N_{\rm A}+N_{\rm B}}\right) + N_{\rm B}\,k_{\rm B}T\,\log\left(\frac{N_{\rm B}}{N_{\rm A}+N_{\rm B}}\right) + \lambda\,\frac{N_{\rm A}N_{\rm B}}{N_{\rm A}+N_{\rm B}} \quad . \tag{2.363}$$

The first four terms on the RHS represent the free energy of the individual component fluids and the entropy of mixing. The last term is an interaction contribution. With $\lambda > 0$, the interaction term prefers that the system be either fully A or fully B. The entropy contribution prefers a mixture, so there is a competition. What is the stable thermodynamic state?

It is useful to write the Gibbs free energy per particle, $g(T, p, x) = G/(N_{\rm A} + N_{\rm B})$, in terms of T, p, and the concentration $x \equiv x_{\rm B} = N_{\rm B}/(N_{\rm A} + N_{\rm B})$ of species B (hence $x_{\rm A} = 1 - x$ is the concentration of species A). Then

$$g(T,p,x) = (1-x)\,\mu^0_{\rm A} + x\,\mu^0_{\rm B} + k_{\rm B}T\Big[x\log x + (1-x)\log(1-x)\Big] + \lambda\,x\,(1-x) \quad . \tag{2.364}$$

In order for the system to be stable against phase separation into relatively A-rich and B-rich regions, we must have that $g(T, p, x)$ be a convex function of x. Our first check should be for a local instability,

i.e. spinodal decomposition. We have

$$\frac{\partial g}{\partial x} = \mu_{\rm B}^0 - \mu_{\rm A}^0 + k_{\rm B}T\,\log\left(\frac{x}{1-x}\right) + \lambda\,(1-2x) \tag{2.365}$$

and

$$\frac{\partial^2 g}{\partial x^2} = \frac{k_{\rm B}T}{x} + \frac{k_{\rm B}T}{1-x} - 2\lambda \quad . \tag{2.366}$$

The spinodal is given by the solution to the equation $\partial^2 g/\partial x^2 = 0$, which is

$$T^*(x) = \frac{2\lambda}{k_{\rm B}}\,x\,(1-x) \quad . \tag{2.367}$$

Since $x\,(1-x)$ achieves its maximum value of $\frac{1}{4}$ at $x = \frac{1}{2}$, we have $T^* \le \lambda/2k_{\rm B}$.

In fig. 2.30 we sketch the free energy $g(T,p,x)$ *versus* x for three representative temperatures. For $T > \lambda/2k_{\rm B}$, the free energy is everywhere convex in x. When $T < \lambda/2k_{\rm B}$, the free energy resembles the blue curve in fig. 2.30, and the system is unstable to phase separation. The two phases are said to be *immiscible*, or, equivalently, there exists a *solubility gap*. To determine the coexistence curve, we perform a Maxwell construction, writing

$$\frac{g(x_2)-g(x_1)}{x_2-x_1} = \left.\frac{\partial g}{\partial x}\right|_{x_1} = \left.\frac{\partial g}{\partial x}\right|_{x_2} \quad . \tag{2.368}$$

Here, x_1 and x_2 are the boundaries of the two phase region. These equations admit a symmetry of $x \leftrightarrow 1-x$, hence we can set $x = x_1$ and $x_2 = 1-x$. We find

$$g(1-x) - g(x) = (1-2x)\left(\mu_{\rm B}^0 - \mu_{\rm A}^0\right) \quad , \tag{2.369}$$

and invoking eqns. 2.368 and 2.365 we obtain the solution

$$T_{\rm coex}(x) = \frac{\lambda}{k_{\rm B}} \cdot \frac{1-2x}{\log\left(\frac{1-x}{x}\right)} \quad . \tag{2.370}$$

The phase diagram for the binary system is shown in fig. 2.32. For $T < T^*(x)$, the system is unstable, and spinodal decomposition occurs. For $T^*(x) < T < T_{\rm coex}(x)$, the system is *metastable*, just like the van der Waals gas in its corresponding regime. Real binary solutions behave qualitatively like the model discussed here, although the coexistence curve is generally not symmetric under $x \leftrightarrow 1-x$, and the single phase region extends down to low temperatures for $x \approx 0$ and $x \approx 1$. If λ itself is temperature-dependent, there can be multiple solutions to eqns. 2.367 and 2.370. For example, one could take

$$\lambda(T) = \frac{\lambda_0\,T^2}{T^2 + T_0^2} \quad . \tag{2.371}$$

In this case, $k_{\rm B}T > \lambda$ at both high and low temperatures, and we expect the single phase region to be *reentrant*. Such a phenomenon occurs in water-nicotine mixtures, for example.

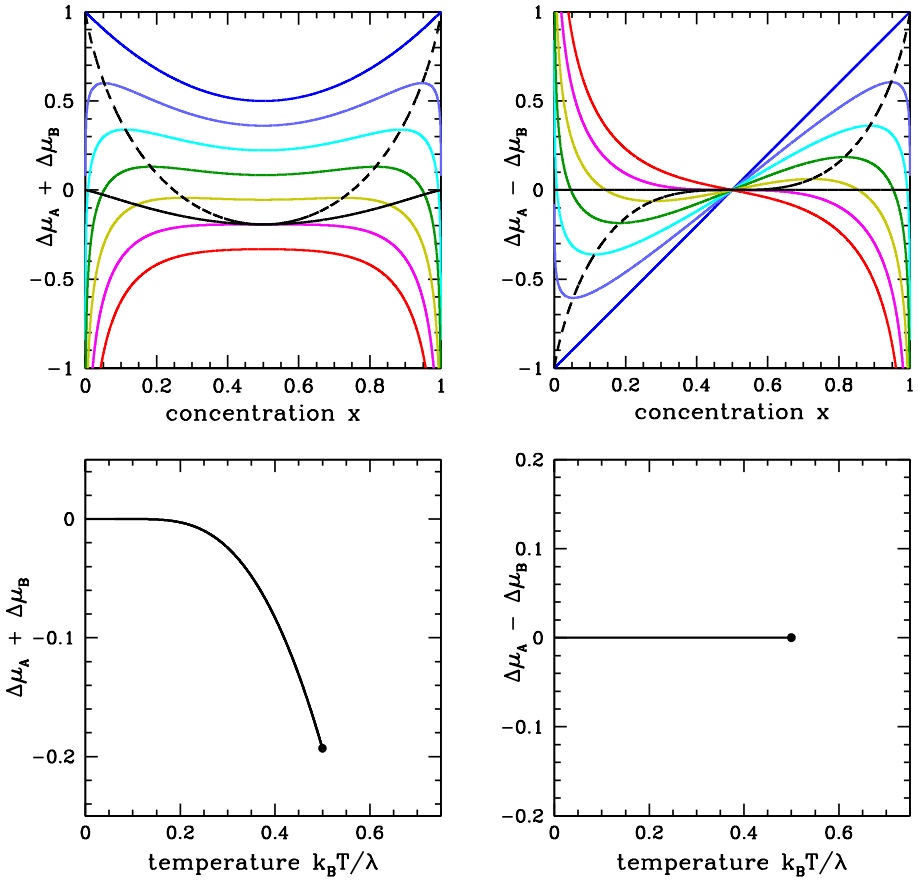


Figure 2.31: Upper panels: chemical potential shifts $\Delta\mu_\pm = \Delta\mu_{\rm A} \pm \Delta\mu_{\rm B}$ *versus* concentration $x = x_{\rm B}$. The dashed black line is the spinodal, and the solid black line the coexistence boundary. Temperatures range from $T = 0$ (dark blue) to $T = 0.6\,\lambda/k_{\rm B}$ (red) in units of $0.1\,\lambda/k_{\rm B}$. Lower panels: phase diagram in the $(T, \Delta\mu_\pm)$ planes. The black dot is the critical point.

It is instructive to consider the phase diagram in the (T, μ) plane. We define the chemical potential shifts,

$$\Delta\mu_{\rm A} \equiv \mu_{\rm A} - \mu_{\rm A}^0 = k_{\rm B}T\log(1-x) + \lambda\,x^2 \tag{2.372}$$

$$\Delta\mu_{\rm B} \equiv \mu_{\rm B} - \mu_{\rm B}^0 = k_{\rm B}T\log x + \lambda\,(1-x)^2 \quad , \tag{2.373}$$

and their sum and difference, $\Delta\mu_\pm \equiv \Delta\mu_{\rm A} \pm \Delta\mu_{\rm B}$. From the Gibbs-Duhem relation, we know that we can write $\mu_{\rm B}$ as a function of T, p, and $\mu_{\rm A}$. Alternately, we could write $\Delta\mu_\pm$ in terms of T, p, and $\Delta\mu_\mp$, so we can choose which among $\Delta\mu_+$ and $\Delta\mu_-$ we wish to use in our phase diagram. The results are plotted in fig. 2.31. It is perhaps easiest to understand the phase diagram in the $(T, \Delta\mu_-)$ plane. At low temperatures, below $T = T_{\rm c} = \lambda/2k_{\rm B}$, there is a first order phase transition at $\Delta\mu_- = 0$. For $T < T_{\rm c} = \lambda/2k_{\rm B}$ and $\Delta\mu_- = 0^+$, *i.e.* infinitesimally positive, the system is in the A-rich phase, but for $\Delta\mu_- = 0^-$, *i.e.* infinitesimally negative, it is B-rich. The concentration $x = x_{\rm B}$ changes discontinuously across the phase boundary. The critical point lies at $(T, \Delta\mu_-) = (\lambda/2k_{\rm B}\,,\,0)$.

If we choose $N = N_{\rm A} + N_{\rm B}$ to be the extensive variable, then fixing N means $dN_{\rm A} + dN_{\rm B} = 0$. So at fixed

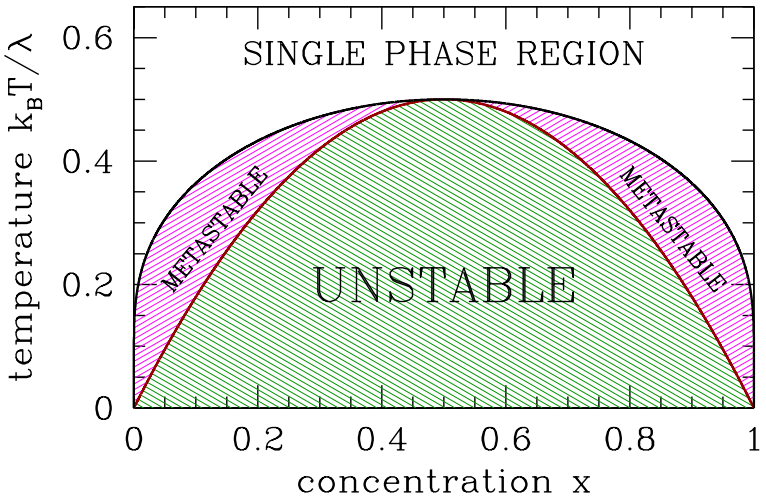


Figure 2.32: Phase diagram for the binary system. The black curve is the coexistence curve, and the dark red curve is the spinodal. A-rich material is to the left and B-rich to the right.

T and p,

$$dG\big|_{T,p} = \mu_{\rm A}\,dN_{\rm A} + \mu_{\rm B}\,dN_{\rm B} \qquad \Rightarrow \qquad dg\big|_{T,p} = \big(\mu^0_{\rm B} - \mu^0_{\rm A} - \Delta\mu_-\big)dx \quad . \tag{2.374}$$

Since $\Delta\mu_-(x,T) = \varphi(x,T) - \varphi(1-x,T) = -\Delta\mu_-(1-x,T)$, where $\varphi(x,T) = \lambda x - k_{\rm B}T\log x$, we have that the coexistence boundary in the (x,Δ_-) plane is simply the line $\Delta\mu_- = 0$, because $\int\limits_x^{1-x} dx'\,\Delta\mu_-(x',T) = 0$.

Note also that there is no two-phase region in the $(T,\Delta\mu)$ plane; the phase boundary in this plane is a curve which terminates at a critical point. As we saw in §2.11, the same situation pertains in single component (p,v,T) systems. That is, the phase diagram in the (p,v) or (T,v) plane contains two-phase regions, but in the (p,T) plane the boundaries between phases are one-dimensional curves. Any two-phase behavior is confined to these curves, where the thermodynamic potentials are singular.

The phase separation can be seen in a number of systems. A popular example involves mixtures of water and ouzo or other anise-based liqueurs, such as arak and absinthe. Starting with the pure liqueur ($x = 1$), and at a temperature below the coexistence curve maximum, the concentration is diluted by adding water. Follow along on fig. 2.32 by starting at the point $(x = 1\,,\ k_{\rm B}T/\lambda = 0.4)$ and move to the left. Eventually, one hits the boundary of the two-phase region. At this point, the mixture turns milky, due to the formation of large droplets of the pure phases on either side of coexistence region which scatter light, a process known as *spontaneous emulsification*[30]. As one continues to dilute the solution with more water, eventually one passes all the way through the coexistence region, at which point the solution becomes clear once again, and described as a single phase.

What happens if $\lambda < 0$? In this case, both the entropy and the interaction energy prefer a mixed phase, and there is no instability to phase separation. The two fluids are said to be *completely miscible*. An example would be benzene, C_6H_6, and toluene, C_7H_8 (*i.e.* $C_6H_5CH_3$). The phase diagram would be blank, with no phase boundaries below the boiling transition, because the fluid could exist as a mixture

[30] An emulsion is a mixture of two or more immiscible liquids.

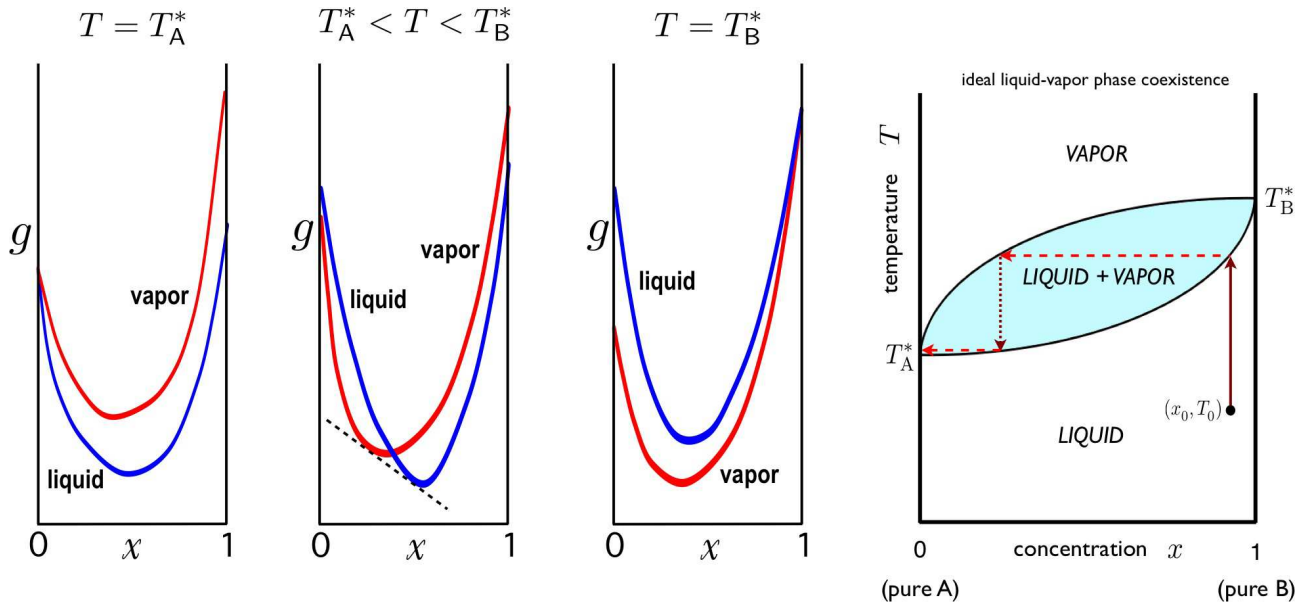


Figure 2.33: Gibbs free energy per particle g for an ideal binary solution for temperatures $T \in [T_A^*, T_B^*]$. The Maxwell construction is shown for the case $T_A^* < T < T_B^*$. Right: phase diagram, showing two-phase region and distillation sequence in (x, T) space.

in any proportion.

Any fluid will eventually boil if the temperature is raised sufficiently high. Let us assume that the boiling points of our A and B fluids are $T_{A,B}^*$, and without loss of generality let us take $T_A^* < T_B^*$ at some given fixed pressure[31]. This means $\mu_A^L(T_A^*, p) = \mu_A^V(T_A^*, p)$ and $\mu_B^L(T_B^*, p) = \mu_B^V(T_B^*, p)$. What happens to the mixture? We begin by writing the free energies of the mixed liquid and mixed vapor phases as

$$g_L(T, p, x) = (1-x)\,\mu_A^L(T, p) + x\,\mu_B^L(T, p) + k_B T\Big[x \log x + (1-x)\log(1-x)\Big] + \lambda_L\, x(1-x) \tag{2.375}$$

$$g_V(T, p, x) = (1-x)\,\mu_A^V(T, p) + x\,\mu_B^V(T, p) + k_B T\Big[x \log x + (1-x)\log(1-x)\Big] + \lambda_V\, x(1-x) \quad . \tag{2.376}$$

Typically $\lambda_V \approx 0$. Consider these two free energies as functions of the concentration x, at fixed T and p. If the curves never cross, and $g_L(x) < g_V(x)$ for all $x \in [0, 1]$, then the liquid is always the state of lowest free energy. This is the situation in the first panel of fig. 2.33. Similarly, if $g_V(x) < g_L(x)$ over this range, then the mixture is in the vapor phase throughout. What happens if the two curves cross at some value of x? This situation is depicted in the second panel of fig. 2.33. In this case, there is always a Maxwell construction which lowers the free energy throughout some range of concentration, *i.e.* the system undergoes phase separation.

In an *ideal fluid*, we have $\lambda_L = \lambda_V = 0$, and setting $g_L = g_V$ requires

$$(1-x)\,\Delta\mu_A(T, p) + x\,\Delta\mu_B(T, p) = 0 \quad , \tag{2.377}$$

[31] We assume the boiling temperatures are not exactly equal.

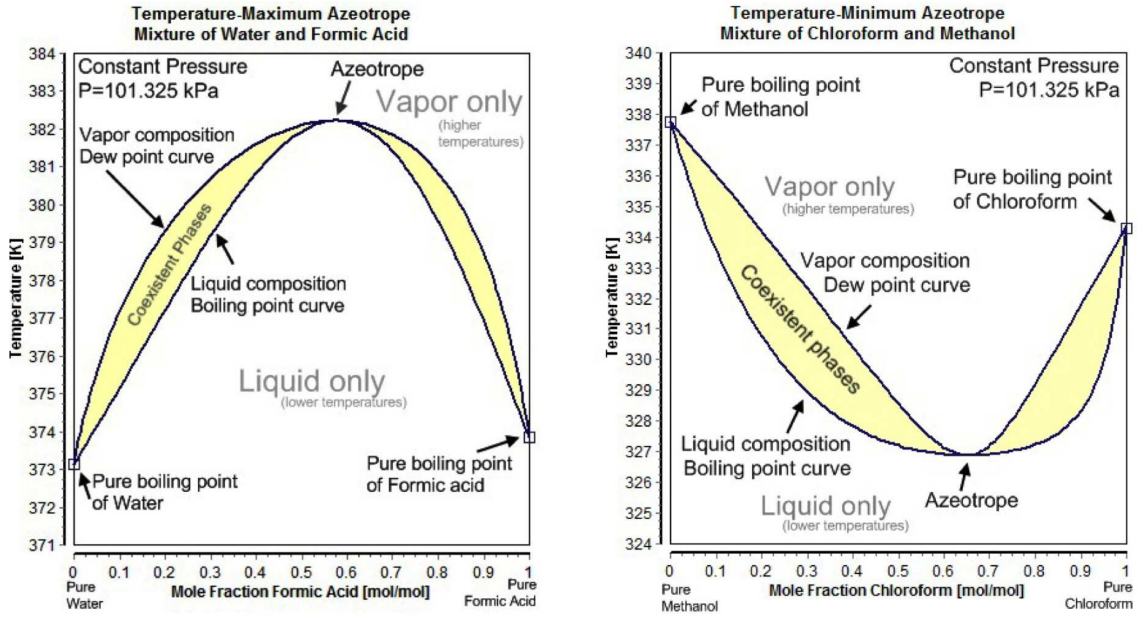


Figure 2.34: Negative (left) and positive (right) azeotrope phase diagrams. From *Wikipedia*.

where $\Delta\mu_{\mathsf{A/B}}(T,p) = \mu^{\rm L}_{\mathsf{A/B}}(T,p) - \mu^{\rm V}_{\mathsf{A/B}}(T,p)$. Expanding the chemical potential about a given temperature T^*,

$$\mu(T,p) = \mu(T^*,p) - s(T^*,p)\,(T-T^*) - \frac{c_p(T^*,p)}{2T^*}\,(T-T^*)^2 + \dots \quad , \tag{2.378}$$

where we have used the fact that $(\partial\mu/\partial T)_{p,N} = -\partial S/\partial N_{T,p} = -s(T,p)$ is the entropy per particle, and $(\partial s/\partial T)_{p,N} = c_p/T$. Thus, expanding $\Delta\mu_{\mathsf{A/B}}$ about $T^*_{\mathsf{A/B}}$, we have

$$\begin{aligned}\Delta\mu_{\mathsf{A}} &\equiv \mu^{\rm L}_{\mathsf{A}} - \mu^{\rm V}_{\mathsf{A}} = (s^{\rm V}_{\mathsf{A}} - s^{\rm L}_{\mathsf{A}})(T - T^*_{\mathsf{A}}) + \frac{c^{\rm V}_{p,\mathsf{A}} - c^{\rm L}_{p,\mathsf{A}}}{2T^*_{\mathsf{A}}}\,(T-T^*_{\mathsf{A}})^2 + \dots \\ \Delta\mu_{\mathsf{B}} &\equiv \mu^{\rm L}_{\mathsf{B}} - \mu^{\rm V}_{\mathsf{B}} = (s^{\rm V}_{\mathsf{B}} - s^{\rm L}_{\mathsf{B}})(T - T^*_{\mathsf{B}}) + \frac{c^{\rm V}_{p,\mathsf{B}} - c^{\rm L}_{p,\mathsf{B}}}{2T^*_{\mathsf{B}}}\,(T-T^*_{\mathsf{B}})^2 + \dots\end{aligned} \tag{2.379}$$

We assume $s^{\rm V}_{\mathsf{A/B}} > s^{\rm L}_{\mathsf{A/B}}$, *i.e.* the vapor phase has greater entropy per particle. Thus, $\Delta\mu_{\mathsf{A/B}}(T)$ changes sign from negative to positive as T rises through $T^*_{\mathsf{A/B}}$. If we assume that these are the *only* sign changes for $\Delta\mu_{\mathsf{A/B}}(T)$ at fixed p, then eqn. 2.377 can only be solved for $T \in [T^*_{\mathsf{A}}, T^*_{\mathsf{B}}]$. This immediately leads to the phase diagram in the rightmost panel of fig. 2.33.

According to the Gibbs phase rule, with $\mathsf{c} = 2$, two-phase equilibrium ($\varphi = 2$) occurs along a subspace of dimension $d_{\rm PE} = 2 + \mathsf{c} - \varphi = 2$. Thus, if we fix the pressure p and the concentration $x = x_{\rm B}$, liquid-gas equilibrium occurs at a particular temperature T^*, known as the boiling point. Since the liquid and the vapor with which it is in equilibrium at T^* may have different composition, *i.e.* different values of x, one may *distill* the mixture to separate the two pure substances, as follows. First, given a liquid mixture of A and B, we bring it to boiling, as shown in the rightmost panel of fig. 2.33. The vapor is at a different concentration x than the liquid (a lower value of x if the boiling point of pure A is less than that of pure

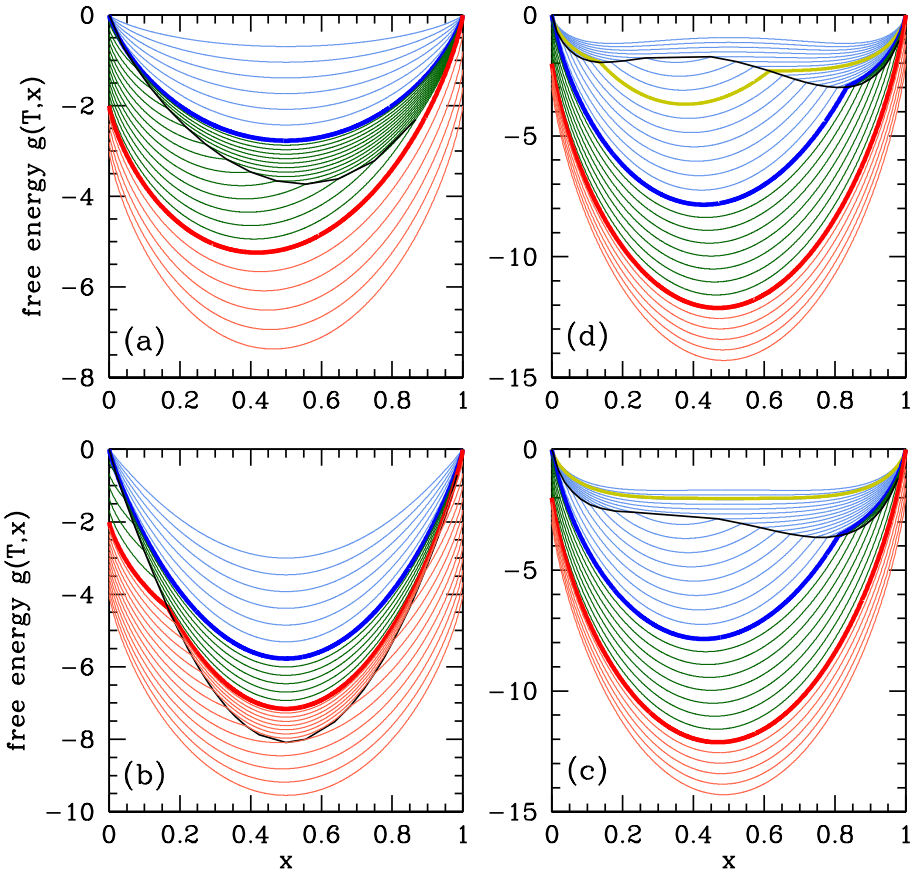


Figure 2.35: Free energies *before Maxwell constructions* for a binary fluid mixture in equilibrium with a vapor ($\lambda_{\rm V} = 0$). Panels show (a) $\lambda_{\rm L} = 0$ (ideal fluid), (b) $\lambda_{\rm L} < 0$ (miscible fluid; negative azeotrope), (c) $\lambda^{\rm L}_{\rm AB} > 0$ (positive azeotrope), (d) $\lambda^{\rm L}_{\rm AB} > 0$ (heteroazeotrope). Thick blue and red lines correspond to temperatures $T^*_{\rm A}$ and $T^*_{\rm B}$, respectively, with $T^*_{\rm A} < T^*_{\rm B}$. Thin blue and red curves are for temperatures outside the range $[T^*_{\rm A}, T^*_{\rm B}]$. The black curves mark the crossings of the liquid and vapor free energy curves, where $g_{\rm L} = g_{\rm V}$. Before the common-tangent construction, the lower envelope of these curves is continuous but generally has a discontinuous slope. The yellow curve in (d) corresponds to the coexistence temperature for the fluid mixture. In this case the azeotrope forms within the coexistence region.

B, as shown). If we collect the vapor, the remaining fluid is at a higher value of x. The collected vapor is then captured and then condensed, forming a liquid at the lower x value. This is then brought to a boil, and the resulting vapor is drawn off and condensed, *etc.* The result is a purified A state. The remaining liquid is then at a higher B concentration. By repeated boiling and condensation, A and B can be separated. For liquid-vapor transitions, the upper curve, representing the lowest temperature at a given concentration for which the mixture is a homogeneous vapor, is called the *dew point curve*. The lower curve, representing the highest temperature at a given concentration for which the mixture is a homogeneous liquid, is called the *bubble point curve*. The same phase diagram applies to liquid-solid mixtures where both phases are completely miscible. In that case, the upper curve is called the *liquidus*, and the lower curve the *solidus*.

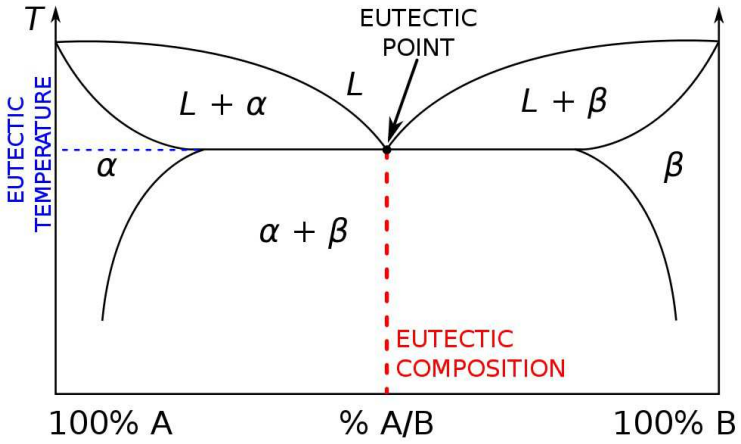


Figure 2.36: Phase diagram for a eutectic mixture in which a liquid L is in equilibrium with two solid phases α and β. The same phase diagram holds for heteroazeotropes, where a vapor is in equilibrium with two liquid phases.

When a homogeneous liquid or vapor at concentration x is heated or cooled to a temperature T such that (x, T) lies within the two-phase region, the mixture phase separates into the two end components $(x^*_{\rm L}, T)$ and $(x^*_{\rm V}, T)$, which lie on opposite sides of the boundary of the two-phase region, at the same temperature. The locus of points at constant T joining these two points is called the *tie line*. To determine how much of each of these two homogeneous phases separates out, we use particle number conservation. If $\eta_{\rm L,V}$ is the fraction of the homogeneous liquid and homogeneous vapor phases present, then $\eta_{\rm L} x^*_{\rm L} + \eta_{\rm V} x^*_{\rm V} = x$, which says $\eta_{\rm L} = (x - x^*_{\rm V})/(x^*_{\rm L} - x^*_{\rm V})$ and $\eta_{\rm V} = (x - x^*_{\rm L})/(x^*_{\rm V} - x^*_{\rm L})$. This is known as the *lever rule*.

For many binary mixtures, the boiling point curve is as shown in fig. 2.34. Such cases are called *azeotropes*. For *negative azeotropes*, the maximum of the boiling curve lies above both $T^*_{\rm A,B}$. The free energy curves for this case are shown in panel (b) of fig. 2.35. For $x < x^*$, where x^* is the azeotropic composition, one can distill A but not B. Similarly, for $x > x^*$ one can distill B but not A. The situation is different for *positive azeotropes*, where the minimum of the boiling curve lies below both $T^*_{\rm A,B}$, corresponding to the free energy curves in panel (c) of fig. 2.35. In this case, distillation (*i.e.* condensing and reboiling the collected vapor) from either side of x^* results in the azeotrope. One can of course collect the fluid instead of the vapor. In general, for both positive and negative azeotropes, starting from a given concentration x, one can only arrive at pure A plus azeotrope (if $x < x^*$) or pure B plus azeotrope (if $x > x^*$). Ethanol (C_2H_5OH) and water (H_2O) form a positive azeotrope which is 95.6% ethanol and 4.4% water by weight. The individual boiling points are $T^*_{\rm C_2H_5OH} = 78.4^\circ{\rm C}$, $T^*_{\rm H_2O} = 100^\circ{\rm C}$, while the azeotrope boils at $T^*_{\rm AZ} = 78.2^\circ{\rm C}$. No amount of distillation of this mixture can purify ethanol beyond the 95.6% level. To go beyond this level of purity, one must resort to *azeotropic distillation*, which involves introducing another component, such as benzene (or a less carcinogenic additive), which alters the molecular interactions.

To model the azeotrope system, we need to take $\lambda_{\rm L} \neq 0$, in which case one can find *two* solutions to the energy crossing condition $g_{\rm V}(x) = g_{\rm L}(x)$. With two such crossings come two Maxwell constructions, hence the phase diagrams in fig. 2.34. *Generally*, negative azeotropes are found in systems with $\lambda_{\rm L} < 0$,

whereas positive azeotropes are found when $\lambda_{\rm L} > 0$. As we've seen, such repulsive interactions between the A and B components in general lead to a phase separation below a coexistence temperature $T_{\rm COEX}(x)$ given by eqn. 2.370. What happens if the minimum boiling point lies within the coexistence region? This is the situation depicted in panel (d) of fig. 2.35. The system is then a liquid/vapor version of the solid/liquid *eutectic* (see fig. 2.36), and the minimum boiling point mixture is called a *heteroazeotrope*.

2.13 Some Concepts in Thermochemistry

2.13.1 Chemical reactions and the law of mass action

Suppose we have a chemical reaction among c species, written as

$$\zeta_1 \, {\rm A}_1 + \zeta_2 \, {\rm A}_2 + \cdots + \zeta_{\rm c} \, {\rm A}_{\rm c} = 0 \quad , \tag{2.380}$$

where ${\rm A}_a$ represents a chemical formula and ζ_a the corresponding stoichiometric coefficient. For example, we could have

$$-3\,{\rm H}_2 - {\rm N}_2 + 2\,{\rm NH}_3 = 0 \qquad (3\,{\rm H}_2 + {\rm N}_2 \rightleftharpoons 2\,{\rm NH}_3) \tag{2.381}$$

for which

$$\zeta({\rm H}_2) = -3 \quad , \quad \zeta({\rm N}_2) = -1 \quad , \quad \zeta({\rm NH}_3) = 2 \quad . \tag{2.382}$$

When $\zeta_a > 0$, the corresponding ${\rm A}_a$ is a *product*; when $\zeta_a < 0$, the corresponding ${\rm A}_a$ is a *reactant*. The bookkeeping of the coefficients ζ_a which ensures conservation of each individual species of atom in the reaction(s) is known as *stoichiometry*[32].

Now we ask: what are the conditions for equilibrium? At constant T and p, which is typical for many chemical reactions, the conditions are that $G\big(T, p, \{N_a\}\big)$ be a minimum. Now

$$dG = -S\,dT + V\,dp + \sum_a \mu_a \, dN_a \quad , \tag{2.383}$$

[32] Antoine Lavoisier, the "father of modern chemistry", made pioneering contributions in both chemistry and biology. In particular, he is often credited as the progenitor of stoichiometry. An aristocrat by birth, Lavoisier was an administrator of the *Ferme générale*, an organization in pre-revolutionary France which collected taxes on behalf of the king. At the age of 28, Lavoisier married Marie-Anne Pierette Paulze, the 13-year-old daughter of one of his business partners. She would later join her husband in his research, and she played a role in his disproof of the phlogiston theory of combustion. The phlogiston theory was superseded by Lavoisier's work, where, based on contemporary experiments by Joseph Priestley, he correctly identified the pivotal role played by oxygen in both chemical and biological processes (*i.e.* respiration). Despite his fame as a scientist, Lavoisier succumbed to the Reign of Terror. His association with the *Ferme générale*, which collected taxes from the poor and the downtrodden, was a significant liability in revolutionary France. Furthermore – and let this be a lesson to all of us – Lavoisier had unwisely ridiculed a worthless pseudoscientific pamphlet, ostensibly on the physics of fire, and its author, Jean-Paul Marat. Marat was a journalist with scientific pretensions, but apparently little in the way of scientific talent or acumen. Lavoisier effectively blackballed Marat's candidacy to the French Academy of Sciences, and the time came when Marat sought revenge. Marat was instrumental in getting Lavoisier and other members of the *Ferme générale* arrested on charges of counterrevolutionary activities, and on May 8, 1794, after a trial lasting less than a day, Lavoisier was guillotined. Along with Fourier and Carnot, Lavoisier's name is one of the 72 engraved on the Eiffel Tower.

so if we let the reaction go forward, we have $dN_a = \zeta_a$, and if it runs in reverse we have $dN_a = -\zeta_a$. Thus, setting $dT = dp = 0$, we have the equilibrium condition $\sum_{a=1}^{\mathsf{c}} \zeta_a \, \mu_a = 0$.

Let us investigate the consequences of this relation for ideal gases. From eqn. 2.332 and the relation $\mu_a = -T(\partial S/\partial N_a)$, the chemical potential of the $a^{\rm th}$ species is of the form

$$\mu_a(T,p) = k_{\rm B}T \log p_a + k_{\rm B}T \log \psi_a(T) \quad , \tag{2.384}$$

where each $\psi_a(T)$ has units of inverse pressure[33]. Here $p_a = p x_a$ is the partial pressure of species a, where $x_a = N_a / \sum_b N_b$ is its dimensionless concentration[34]. In equilibrium we must have

$$\sum_{a=1}^{\mathsf{c}} \zeta_a \, \mu_a = k_{\rm B}T \sum_a \zeta_a \Big[\log x_a + \log p + \log \psi_a(T) \Big] = 0 \quad . \tag{2.385}$$

Exponentiating, we obtain the *law of mass action*:

$$\prod_a x_a^{\zeta_a} = \prod_a \big(p \, \psi_a(T) \big)^{-\zeta_a} \equiv \kappa(p,T) \quad . \tag{2.386}$$

The quantity $\kappa(p,T)$ is called the *equilibrium constant*. When κ is large, the LHS of the above equation is large. This favors maximal concentration x_a for the products ($\zeta_a > 0$) and minimal concentration x_a for the reactants ($\zeta_a < 0$). This means that the equation $\mathsf{REACTANTS} \rightleftharpoons \mathsf{PRODUCTS}$ is shifted to the right, *i.e.* the products are plentiful and the reactants are scarce. When κ is small, the LHS is small and the reaction is shifted to the left, *i.e.* the reactants are plentiful and the products are scarce. Remember we are describing *equilibrium conditions* here. Now we observe that reactions for which $\sum_a \zeta_a > 0$ shift to the left with increasing pressure and shift to the right with decreasing pressure, while reactions for which $\sum_a \zeta_a < 0$ the situation is reversed: they shift to the right with increasing pressure and to the left with decreasing pressure. When $\sum_a \zeta_a = 0$ there is no shift upon increasing or decreasing pressure.

The rate at which the equilibrium constant changes with temperature is given by

$$\left(\frac{\partial \log \kappa}{\partial T} \right)_p = -\sum_a \zeta_a \, \frac{\partial \log \psi_a(T)}{\partial T} \quad . \tag{2.387}$$

Now from eqn. 2.384 we have that the enthalpy per particle for species a is

$$\mathsf{h}_a = \mu_a - T \left(\frac{\partial \mu_a}{\partial T} \right)_{p_a} \quad , \tag{2.388}$$

since $\mathsf{H} = G + TS$ and $S = -(\partial G/\partial T)_p$. We find

$$\mathsf{h}_a = -k_{\rm B}T^2 \, \frac{\partial \log \psi_a(T)}{\partial T} \quad , \tag{2.389}$$

and thus

$$\left(\frac{\partial \log \kappa}{\partial T} \right)_p = \frac{\sum_i \zeta_a \, \mathsf{h}_a}{k_{\rm B}T^2} = \frac{\Delta \mathsf{h}}{k_{\rm B}T^2} \quad , \tag{2.390}$$

[33] In terms of the functions $\phi_a(T)$ from eqn. 2.332, one has $\log \psi_a(T) = -\phi_a(T)/k_{\rm B} - \log(k_{\rm B}T/e)$.

[34] Chemists sometimes write $x_a = [{\rm A}_a]$ for the concentration of species a.

where $\Delta\mathsf{h}$ is the enthalpy of the reaction, which is the heat absorbed or emitted as a result of the reaction.

When $\Delta\mathsf{h} > 0$ the reaction is *endothermic* and the yield increases with increasing T. When $\Delta\mathsf{h} < 0$ the reaction is *exothermic* and the yield decreases with increasing T.

As an example, consider the gas phase reaction $\mathrm{H_2} + \mathrm{I_2} \rightleftharpoons 2\,\mathrm{HI}$. We have

$$\zeta(\mathrm{H_2}) = -1 \quad , \quad \zeta(\mathrm{I_2}) = -1 \qquad\qquad \zeta(\mathrm{HI}) = 2 \quad . \tag{2.391}$$

Suppose our initial system consists of ν_1^0 moles of $\mathrm{H_2}$, $\nu_2^0 = 0$ moles of $\mathrm{I_2}$, and ν_3^0 moles of undissociated HI . These mole numbers determine the initial concentrations x_a^0, where $x_a = \nu_a / \sum_b \nu_b$. Define

$$\alpha \equiv \frac{x_3^0 - x_3}{x_3^0} \quad , \tag{2.392}$$

in which case we have

$$x_1 = x_1^0 + \tfrac{1}{2}\alpha x_3^0 \qquad , \qquad x_2 = \tfrac{1}{2}\alpha x_3^0 \qquad , \qquad x_3 = \frac{x_3^0}{1+\alpha} \quad . \tag{2.393}$$

Then the law of mass action gives

$$\frac{x_3^2}{x_1 x_2} = \frac{4\,(1-\alpha)^2}{\alpha(\alpha + 2r)} = \kappa \quad . \tag{2.394}$$

where $r \equiv x_1^0/x_3^0 = \nu_1^0/\nu_3^0$. This yields a quadratic equation, which can be solved to find $\alpha(\kappa, r)$. Note that $\kappa = \kappa(T)$ for this reaction since $\sum_a \zeta_a = 0$. The formation of HI in this gas phase reaction is exothermic: $\Delta\mathsf{h} < 0$.

2.13.2 Enthalpy of formation

Most chemical reactions take place under constant pressure. The heat Q_{if} associated with a given isobaric process is

$$Q_{\mathrm{if}} = \int_{\mathrm{i}}^{\mathrm{f}} dE + \int_{\mathrm{i}}^{\mathrm{f}} p\,dV = (E_{\mathrm{f}} - E_{\mathrm{i}}) + p\,(V_{\mathrm{f}} - V_{\mathrm{i}}) = \mathsf{H}_{\mathrm{f}} - \mathsf{H}_{\mathrm{i}} \quad , \tag{2.395}$$

where H is the *enthalpy*,

$$\mathsf{H} = E + pV \quad . \tag{2.396}$$

Note that the enthalpy H is a state function, since E is a state function and p and V are state variables. Hence, we can meaningfully speak of changes in enthalpy: $\Delta\mathsf{H} = \mathsf{H}_{\mathrm{f}} - \mathsf{H}_{\mathrm{i}}$. If $\Delta\mathsf{H} < 0$ for a given reaction, we call it *exothermic* – this is the case when $Q_{\mathrm{if}} < 0$ and thus heat is transferred to the surroundings. Such reactions can occur spontaneously, and, in really fun cases, can produce explosions. The combustion of fuels is always exothermic. If $\Delta\mathsf{H} > 0$, the reaction is called *endothermic*, and the system absorbs heat under conditions of constant pressure. Photosynthesis is an example of an endothermic reaction. In general, a reaction may proceed spontaneously provided that $\Delta G = \Delta\mathsf{H} - T\Delta S < 0$.

Suppose we have two reactions

$$A + B \xrightarrow{(\Delta\mathsf{H})_1} C \tag{2.397}$$

Formula	Name	State	ΔH_f^0 kJ/mol	Formula	Name	State	ΔH_f^0 kJ/mol
Ag	Silver	crystal	0.0	$NiSO_4$	Nickel sulfate	crystal	-872.9
C	Graphite	crystal	0.0	Al_2O_3	Aluminum oxide	crystal	-1657.7
C	Diamond	crystal	1.9	$Ca_3(PO_4)_2$	Calcium phosphate	solid	-4120.8
O_3	Ozone	gas	142.7	HCN	Hydrogen cyanide	liquid	108.9
H_2O	Water	liquid	-285.8	SF_6	Sulfur hexafluoride	gas	-1220.5
H_3BO_3	Boric acid	crystal	-1094.3	CaF_2	Calcium fluoride	crystal	-1228.0
$ZnSO_4$	Zinc sulfate	crystal	-982.8	$CaCl_2$	Calcium chloride	crystal	-795.4

Table 2.5: Enthalpies of formation of some common substances.

and

$$C + D \xrightarrow{(\Delta H)_2} E \quad . \tag{2.398}$$

Then we may write

$$A + B + D \xrightarrow{(\Delta H)_3} E \quad , \tag{2.399}$$

with

$$(\Delta H)_1 + (\Delta H)_2 = (\Delta H)_3 \quad . \tag{2.400}$$

We can use this additivity of reaction enthalpies to define a *standard molar enthalpy of formation*. We first define the *reference standard state* of a pure substance at a given temperature to be its state (gas, liquid, or solid) at a pressure $p = 1\,\text{bar}$. The *standard reaction enthalpies* at a given temperature are then defined to be the reaction enthalpies when the reactants and products are all in their standard states. Finally, we define the *standard molar enthalpy of formation* $\Delta H_f^0(X)$ of a compound X at temperature T as the reaction enthalpy for the compound X to be produced by its constituents when they are in their standard state. For example, if $X = SO_2$, then we write

$$S + O_2 \xrightarrow{\Delta H_f^0[SO_2]} SO_2 \quad . \tag{2.401}$$

The enthalpy of formation of any *element* in its reference standard state is zero at all temperatures, by definition: $\Delta H_f^0[\text{He}] = \Delta H_f^0[\text{K}] = \Delta H_f^0[\text{Mn}] = 0$, *etc.*

Suppose now we have a reaction

$$a\,A + b\,B \xrightarrow{\Delta H} c\,C + d\,D \quad . \tag{2.402}$$

To compute the reaction enthalpy ΔH, we can imagine forming the components A and B from their standard state constituents. Similarly, we can imagine doing the same for C and D. Since the number of atoms of a given kind is conserved in the process, the constituents of the reactants must be the same as those of the products, we have

$$\Delta H = -a\,\Delta H_f^0(A) - b\,\Delta H_f^0(B) + c\,\Delta H_f^0(C) + d\,\Delta H_f^0(D) \quad . \tag{2.403}$$

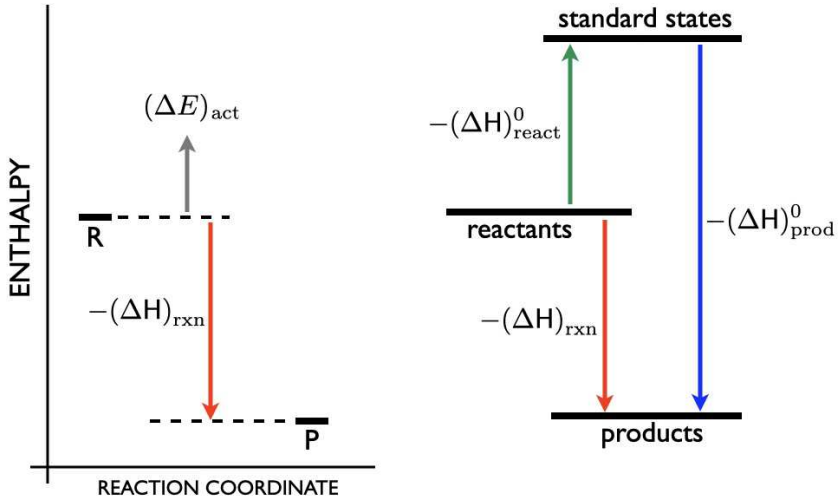


Figure 2.37: Left panel: reaction enthalpy and activation energy (exothermic case shown). Right panel: reaction enthalpy as a difference between enthalpy of formation of reactants and products.

A list of a few enthalpies of formation is provided in table 2.5. Note that the reaction enthalpy is independent of the actual reaction path. That is, the difference in enthalpy between A and B is the same whether the reaction is $A \longrightarrow B$ or $A \longrightarrow X \longrightarrow (Y + Z) \longrightarrow B$. This statement is known as *Hess's Law*.

Note that

$$d{\rm H} = dE + p\,dV + V\,dp = đQ + V\,dp \quad , \tag{2.404}$$

hence

$$C_p = \left(\frac{đQ}{dT}\right)_p = \left(\frac{\partial {\rm H}}{\partial T}\right)_p \quad . \tag{2.405}$$

We therefore have

$${\rm H}(T,p,\nu) = {\rm H}(T_0,p,\nu) + \nu \int\limits_{T_0}^{T} dT'\, c_p(T') \quad . \tag{2.406}$$

For ideal gases, we have $c_p(T) = (1+\frac{1}{2}f)\,R$. For real gases, over a range of temperatures, there are small variations:

$$c_p(T) = \alpha + \beta\,T + \gamma\,T^2 \quad . \tag{2.407}$$

Two examples ($300\,{\rm K} < T < 1500\,{\rm K}$, $p = 1\,{\rm atm}$):

$$\begin{aligned} {\rm O_2}: \quad & \alpha = 25.503\,\frac{\rm J}{\rm mol\,K} \quad , \quad \beta = 13.612\times 10^{-3}\,\frac{\rm J}{\rm mol\,K^2} \quad , \quad \gamma = -42.553\times 10^{-7}\,\frac{\rm J}{\rm mol\,K^3} \\ {\rm H_2O}: \quad & \alpha = 30.206\,\frac{\rm J}{\rm mol\,K} \quad , \quad \beta = 9.936\times 10^{-3}\,\frac{\rm J}{\rm mol\,K^2} \quad , \quad \gamma = 11.14\times 10^{-7}\,\frac{\rm J}{\rm mol\,K^3} \end{aligned}$$

If all the gaseous components in a reaction can be approximated as ideal, then we may write

$$(\Delta {\rm H})_{\rm rxn} = (\Delta E)_{\rm rxn} + \sum_a \zeta_a\,RT \quad , \tag{2.408}$$

bond	enthalpy (kJ/mol)	bond	enthalpy (kJ/mol)	bond	enthalpy (kJ/mol)	bond	enthalpy (kJ/mol)
H – H	436	C – C	348	C – S	259	F – F	155
H – C	412	C = C	612	N – N	163	F – Cl	254
H – N	388	C ≡ C	811	N = N	409	Cl – Br	219
H – O	463	C – N	305	N ≡ N	945	Cl – I	210
H – F	565	C = N	613	N – O	157	Cl – S	250
H – Cl	431	C ≡ N	890	N – F	270	Br – Br	193
H – Br	366	C – O	360	N – Cl	200	Br – I	178
H – I	299	C = O	743	N – Si	374	Br – S	212
H – S	338	C – F	484	O – O	146	I – I	151
H – P	322	C – Cl	338	O = O	497	S – S	264
H – Si	318	C – Br	276	O – F	185	P – P	172
		C – I	238	O – Cl	203	Si – Si	176

Table 2.6: Average bond enthalpies for some common bonds. (*Credit: L. Pauling, The Nature of the Chemical Bond (Cornell Univ. Press, NY, 1960).)*

where the subscript 'rxn' stands for 'reaction'. Here $(\Delta E)_{\rm rxn}$ is the change in energy from reactants to products.

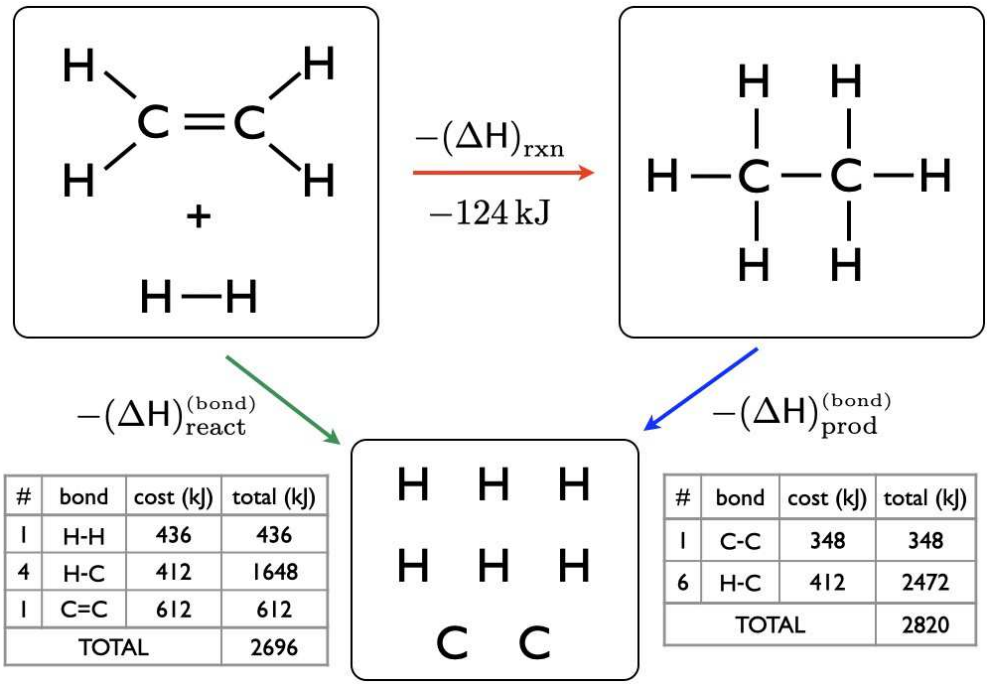
2.13.3 Bond enthalpies

The enthalpy needed to break a chemical bond is called the *bond enthalpy*, $\mathsf{h}[\bullet]$. The bond enthalpy is the energy required to dissociate one mole of gaseous bonds to form gaseous atoms. A table of bond enthalpies is given in Tab. 2.6. Bond enthalpies are endothermic, since energy is required to break chemical bonds. Of course, the actual bond energies can depend on the location of a bond in a given molecule, and the values listed in the table reflect averages over the possible bond environment.

The bond enthalpies in Tab. 2.6 may be used to compute reaction enthalpies. Consider, for example, the reaction $2\,{\rm H_2(g)} + {\rm O_2(g)} \longrightarrow 2\,{\rm H_2O(l)}$. We then have, from the table,

$$\begin{aligned}(\Delta\mathsf{H})_{\rm rxn} &= 2\,\mathsf{h}[{\rm H\!-\!H}] + \mathsf{h}[{\rm O\!=\!O}] - 4\,\mathsf{h}[{\rm H\!-\!O}] \\ &= -483\,{\rm kJ/mol\ O_2} \quad .\end{aligned} \tag{2.409}$$

Thus, 483 kJ of heat would be released for every two moles of $\rm H_2O$ produced, if the $\rm H_2O$ were in the gaseous phase. Since $\rm H_2O$ is liquid at STP, we should also include the condensation energy of the gaseous water vapor into liquid water. At $T = 100^\circ{\rm C}$ the latent heat of vaporization is $\tilde\ell = 2270\,{\rm J/g}$, but at $T = 20^\circ{\rm C}$, one has $\tilde\ell = 2450\,{\rm J/g}$, hence with $M = 18$ we have $\ell = 44.1\,{\rm kJ/mol}$. Therefore, the heat produced by the reaction $2\,{\rm H_2(g)} + {\rm O_2(g)} \rightleftharpoons 2\,{\rm H_2O(l)}$ is $(\Delta H)_{\rm rxn} = -571.2\,{\rm kJ\,/\,mol\ O_2}$. Since the



#	bond	cost (kJ)	total (kJ)
1	H-H	436	436
4	H-C	412	1648
1	C=C	612	612
TOTAL			2696

#	bond	cost (kJ)	total (kJ)
1	C-C	348	348
6	H-C	412	2472
TOTAL			2820

Figure 2.38: Calculation of reaction enthalpy for the hydrogenation of ethene (ethylene), C_2H_4.

reaction produces two moles of water, we conclude that the enthalpy of formation of liquid water at STP is half this value: $\Delta H_f^0[H_2O] = -285.6\,\mathrm{kJ/mol}$.

Hydrogenation of ethene

Hydrogenation is the adding of hydrogen to a carbon-carbon double bond. Consider the hydrogenation of ethene (ethylene): $C_2H_4 + H_2 \rightleftharpoons C_2H_6$. The product is known as ethane. The energy accounting is shown in fig. 2.38. To compute the enthalpies of formation of ethene and ethane from the bond enthalpies, we need one more bit of information, which is the standard enthalpy of formation of $C(g)$ from $C(s)$, since the solid is the standard state at STP. This value is $\Delta H_f^0[C(g)] = 718\,\mathrm{kJ/mol}$. We may now write

$$\begin{aligned} 2\,C(g) + 4\,H(g) &\xrightarrow{-2260\,\mathrm{kJ}} C_2H_4(g) \\ 2\,C(s) &\xrightarrow{1436\,\mathrm{kJ}} 2\,C(g) \\ 2\,H_2(g) &\xrightarrow{872\,\mathrm{kJ}} 4\,H(g) \quad . \end{aligned}$$

Thus, using Hess's law, *i.e.* adding up these reaction equations, we have

$$2\,C(s) + 2\,H_2(g) \xrightarrow{48\,\mathrm{kJ}} C_2H_4(g) \quad .$$

Thus, the formation of ethene is endothermic. For ethane,

$$\begin{aligned} 2\,\mathrm{C(g)} + 6\,\mathrm{H(g)} &\xrightarrow{-2820\,\mathrm{kJ}} \mathrm{C_2H_6(g)} \\ 2\,\mathrm{C(s)} &\xrightarrow{1436\,\mathrm{kJ}} 2\,\mathrm{C(g)} \\ 3\,\mathrm{H_2(g)} &\xrightarrow{1308\,\mathrm{kJ}} 6\,\mathrm{H(g)} \end{aligned}$$

Add 'em up:

$$2\,\mathrm{C(s)} + 3\,\mathrm{H_2(g)} \xrightarrow{-76\,\mathrm{kJ}} \mathrm{C_2H_6(g)} \quad ,$$

which is exothermic. Thus,

$$\mathrm{C_2H_4(g)} + \mathrm{H_2(g)} \xrightarrow{-48\,\mathrm{kJ}} 2\,\mathrm{C(s)} + 3\,\mathrm{H_2(g)} \xrightarrow{-76\,\mathrm{kJ}} \mathrm{C_2H_6(g)} \quad , \tag{2.410}$$

which says

$$\mathrm{C_2H_4(g)} + \mathrm{H_2(g)} \xrightarrow{-124\,\mathrm{kJ}} \mathrm{C_2H_6(g)} \quad . \tag{2.411}$$

The hydrogenation of ethene is thus exothermic. However, there is a high activation energy associated with the intermediate state which prevents the reaction from taking place under normal conditions. This may be circumvented, however, through use of a catalyst, such as a Pt, Pd, or Ni surface.

2.14 Appendix I: Integrating Factors

Suppose we have an inexact differential

$$đW = A_i\,dx_i \quad . \tag{2.412}$$

Here I am adopting the 'Einstein convention' where we sum over repeated indices unless otherwise explicitly stated; $A_i\,dx_i = \sum_i A_i\,dx_i$. An *integrating factor* $\exp\bigl[L(\boldsymbol{x})\bigr]$ is a function which, when divided into $đW$, yields an exact differential:

$$dU = e^{-L}\,đW = \frac{\partial U}{\partial x_i}\,dx_i \quad . \tag{2.413}$$

Clearly we must have

$$\frac{\partial^2 U}{\partial x_i\,\partial x_j} = \frac{\partial}{\partial x_i}\left(e^{-L}\,A_j\right) = \frac{\partial}{\partial x_j}\left(e^{-L}\,A_i\right) \quad . \tag{2.414}$$

Applying the Leibniz rule and then multiplying by e^L yields

$$\frac{\partial A_j}{\partial x_i} - A_j\,\frac{\partial L}{\partial x_i} = \frac{\partial A_i}{\partial x_j} - A_i\,\frac{\partial L}{\partial x_j} \quad . \tag{2.415}$$

If there are K independent variables $\{x_1, \ldots, x_K\}$, then there are $\frac{1}{2}K(K-1)$ independent equations of the above form – one for each distinct (i,j) pair. These equations can be written compactly as

$$\Omega_{ijk}\,\frac{\partial L}{\partial x_k} = F_{ij} \quad , \tag{2.416}$$

where

$$\Omega_{ijk} = A_j\,\delta_{ik} - A_i\,\delta_{jk} \tag{2.417}$$

$$F_{ij} = \frac{\partial A_j}{\partial x_i} - \frac{\partial A_i}{\partial x_j} \quad . \tag{2.418}$$

Note that F_{ij} is antisymmetric, and resembles a field strength tensor, and that $\Omega_{ijk} = -\Omega_{jik}$ is antisymmetric in the first two indices (but is not totally antisymmetric in all three).

Can we solve these $\frac{1}{2}K(K-1)$ coupled equations to find an integrating factor L? In general the answer is *no*. However, when $K = 2$ we can always find an integrating factor. To see why, let's call $x \equiv x_1$ and $y \equiv x_2$. Consider now the ODE

$$\frac{dy}{dx} = -\frac{A_x(x,y)}{A_y(x,y)} \quad . \tag{2.419}$$

This equation can be integrated to yield a one-parameter set of integral curves, indexed by an initial condition. The equation for these curves may be written as $U_c(x,y) = 0$, where c labels the curves. Then along each curve we have

$$\begin{aligned} 0 = \frac{dU_c}{dx} &= \frac{\partial U_c}{\partial x} + \frac{\partial U_c}{\partial y}\,\frac{dy}{dx} \\ &= \frac{\partial U_c}{\partial x} - \frac{A_x}{A_y}\,\frac{\partial U_c}{\partial y} \quad . \end{aligned} \tag{2.420}$$

Thus,

$$\frac{\partial U_c}{\partial x}\,A_y = \frac{\partial U_c}{\partial y}\,A_x \equiv e^{-L} A_x\,A_y \quad . \tag{2.421}$$

This equation defines the integrating factor L:

$$L = -\log\left(\frac{1}{A_x}\,\frac{\partial U_c}{\partial x}\right) = -\log\left(\frac{1}{A_y}\,\frac{\partial U_c}{\partial y}\right) \quad . \tag{2.422}$$

We now have that

$$A_x = e^L\,\frac{\partial U_c}{\partial x} \qquad , \qquad A_y = e^L\,\frac{\partial U_c}{\partial y} \quad , \tag{2.423}$$

and hence

$$e^{-L}\,đW = \frac{\partial U_c}{\partial x}\,dx + \frac{\partial U_c}{\partial y}\,dy = dU_c \quad . \tag{2.424}$$

2.15 Appendix II: Other Thermodynamic Cycles

2.15.1 The Stirling cycle

In §2.5.4 we analyzed the famous Carnot cycle. Many other thermodynamic cycles are commonly used. The Stirling cycle, depicted in fig. 2.39, consists of two isotherms and two isochores. Recall the isothermal ideal gas equation of state, $d(pV) = 0$. Thus, for an ideal gas Stirling cycle, we have

$$p_{\rm A} V_1 = p_{\rm B} V_2 \qquad , \qquad p_{\rm D} V_1 = p_{\rm C} V_2 \quad , \tag{2.425}$$

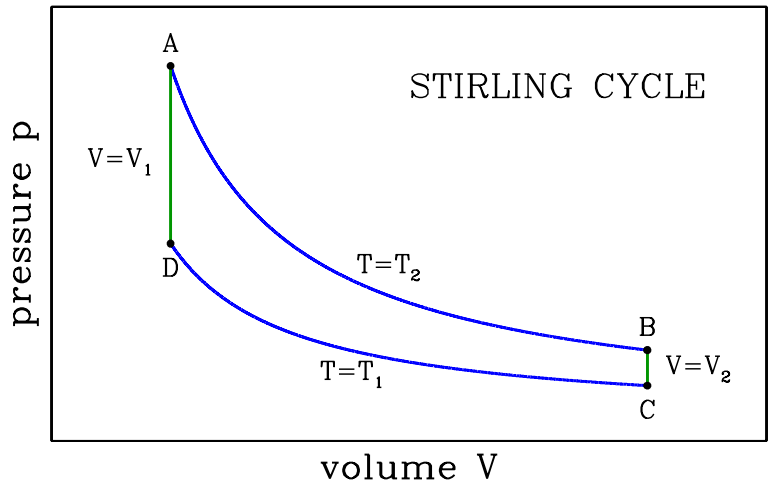


Figure 2.39: A Stirling cycle consists of two isotherms (blue) and two isochores (green).

which says

$$\frac{p_{\rm B}}{p_{\rm A}} = \frac{p_{\rm C}}{p_{\rm D}} = \frac{V_1}{V_2} \quad . \tag{2.426}$$

AB: This isothermal expansion is the power stroke. Assuming ν moles of ideal gas throughout, we have $pV = \nu RT_2 = p_{\rm A}V_1$, hence

$$W_{\rm AB} = \int_{V_1}^{V_2} dV\, \frac{\nu RT_2}{V} = \nu RT_2\, \log\left(\frac{V_2}{V_1}\right) \quad . \tag{2.427}$$

Since AB is an isotherm, we have $E_{\rm A} = E_{\rm B}$, and from $\Delta E_{\rm AB} = 0$ we conclude $Q_{\rm AB} = W_{\rm AB}$.

BC: Isochoric cooling. Since $dV = 0$ we have $W_{\rm BC} = 0$. The energy change is given by

$$\Delta E_{\rm BC} = E_{\rm C} - E_{\rm B} = \frac{\nu R(T_1 - T_2)}{\gamma - 1}, \tag{2.428}$$

which is negative. Since $W_{\rm BC} = 0$, we have $Q_{\rm BC} = \Delta E_{\rm BC}$.

CD: Isothermal compression. Clearly

$$W_{\rm CD} = \int_{V_2}^{V_1} dV\, \frac{\nu RT_1}{V} = -\nu RT_1\, \log\left(\frac{V_2}{V_1}\right) \quad . \tag{2.429}$$

Since CD is an isotherm, we have $E_{\rm C} = E_{\rm D}$, and from $\Delta E_{\rm CD} = 0$ we conclude $Q_{\rm CD} = W_{\rm CD}$.

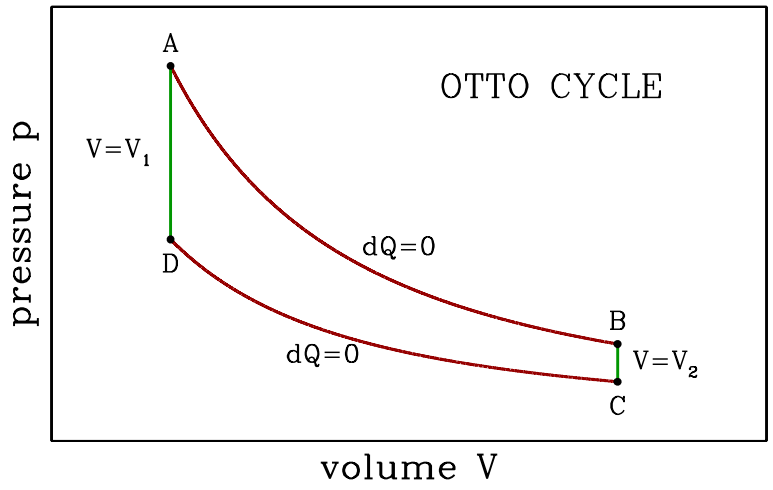


Figure 2.40: An Otto cycle consists of two adiabats (dark red) and two isochores (green).

DA: Isochoric heating. Since $dV = 0$ we have $W_{\rm DA} = 0$. The energy change is given by

$$\Delta E_{\rm DA} = E_{\rm A} - E_{\rm D} = \frac{\nu R(T_2 - T_1)}{\gamma - 1} \quad , \tag{2.430}$$

which is positive, and opposite to $\Delta E_{\rm BC}$. Since $W_{\rm DA} = 0$, we have $Q_{\rm DA} = \Delta E_{\rm DA}$.

We now add up all the work contributions to obtain

$$\begin{aligned} W &= W_{\rm AB} + W_{\rm BC} + W_{\rm CD} + W_{\rm DA} \\ &= \nu R(T_2 - T_1)\, \log\left(\frac{V_2}{V_1}\right) \quad . \end{aligned} \tag{2.431}$$

The cycle efficiency is once again

$$\eta = \frac{W}{Q_{\rm AB}} = 1 - \frac{T_1}{T_2} \quad . \tag{2.432}$$

2.15.2 The Otto and Diesel cycles

The Otto cycle is a rough approximation to the physics of a gasoline engine. It consists of two adiabats and two isochores, and is depicted in fig. 2.40. Assuming an ideal gas, along the adiabats we have $d(pV^\gamma) = 0$. Thus,

$$p_{\rm A}\, V_1^\gamma = p_{\rm B}\, V_2^\gamma \qquad , \qquad p_{\rm D}\, V_1^\gamma = p_{\rm C}\, V_2^\gamma \quad , \tag{2.433}$$

which says

$$\frac{p_{\rm B}}{p_{\rm A}} = \frac{p_{\rm C}}{p_{\rm D}} = \left(\frac{V_1}{V_2}\right)^\gamma \quad . \tag{2.434}$$

AB: Adiabatic expansion, the power stroke. The heat transfer is $Q_{\rm AB} = 0$, so from the First Law we have $W_{\rm AB} = -\Delta E_{\rm AB} = E_{\rm A} - E_{\rm B}$, thus

$$W_{\rm AB} = \frac{p_{\rm A}V_1 - p_{\rm B}V_2}{\gamma - 1} = \frac{p_{\rm A}V_1}{\gamma - 1}\left[1 - \left(\frac{V_1}{V_2}\right)^{\gamma-1}\right] \quad . \tag{2.435}$$

Note that this result can also be obtained from the adiabatic equation of state $pV^\gamma = p_{\rm A}V_1^\gamma$:

$$W_{\rm AB} = \int_{V_1}^{V_2} p\,dV = p_{\rm A}V_1^\gamma \int_{V_1}^{V_2} dV\,V^{-\gamma} = \frac{p_{\rm A}V_1}{\gamma - 1}\left[1 - \left(\frac{V_1}{V_2}\right)^{\gamma-1}\right] \quad . \tag{2.436}$$

BC: Isochoric cooling (exhaust); $dV = 0$ hence $W_{\rm BC} = 0$. The heat $Q_{\rm BC}$ absorbed is then

$$Q_{\rm BC} = E_{\rm C} - E_{\rm B} = \frac{V_2}{\gamma - 1}\left(p_{\rm C} - p_{\rm B}\right) \quad . \tag{2.437}$$

In a realistic engine, this is the stage in which the old burned gas is ejected and new gas is inserted.

CD: Adiabatic compression; $Q_{\rm CD} = 0$ and $W_{\rm CD} = E_{\rm C} - E_{\rm D}$:

$$W_{\rm CD} = \frac{p_{\rm C}V_2 - p_{\rm D}V_1}{\gamma - 1} = -\frac{p_{\rm D}V_1}{\gamma - 1}\left[1 - \left(\frac{V_1}{V_2}\right)^{\gamma-1}\right] \quad . \tag{2.438}$$

DA: Isochoric heating, *i.e.* the combustion of the gas. As with BC we have $dV = 0$, and thus $W_{\rm DA} = 0$. The heat $Q_{\rm DA}$ absorbed by the gas is then

$$Q_{\rm DA} = E_{\rm A} - E_{\rm D} = \frac{V_1}{\gamma - 1}\left(p_{\rm A} - p_{\rm D}\right) \quad . \tag{2.439}$$

The total work done per cycle is then

$$\begin{aligned} W &= W_{\rm AB} + W_{\rm BC} + W_{\rm CD} + W_{\rm DA} \\ &= \frac{(p_{\rm A} - p_{\rm D})V_1}{\gamma - 1}\left[1 - \left(\frac{V_1}{V_2}\right)^{\gamma-1}\right] \quad , \end{aligned} \tag{2.440}$$

and the efficiency is defined to be

$$\eta \equiv \frac{W}{Q_{\rm DA}} = 1 - \left(\frac{V_1}{V_2}\right)^{\gamma-1} \quad . \tag{2.441}$$

The ratio V_2/V_1 is called the *compression ratio*. We can make our Otto cycle more efficient simply by increasing the compression ratio. The problem with this scheme is that if the fuel mixture becomes too hot, it will spontaneously 'preignite', and the pressure will jump up before point D in the cycle is reached. A Diesel engine avoids preignition by compressing the air only, and then later spraying the fuel

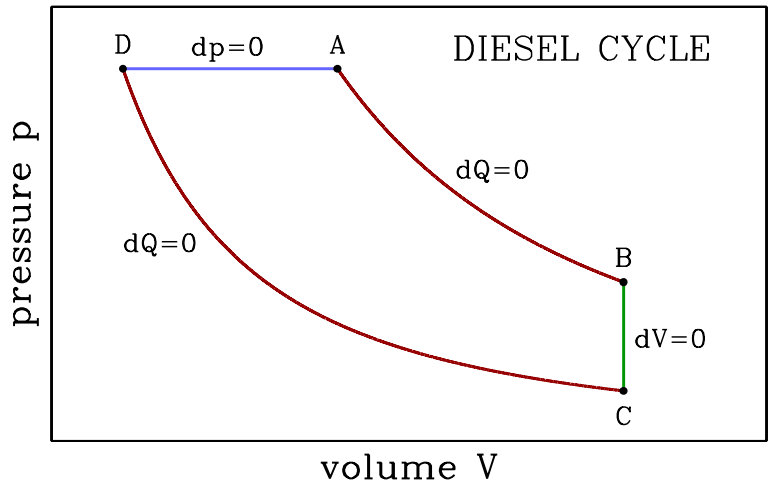


Figure 2.41: A Diesel cycle consists of two adiabats (dark red), one isobar (light blue), and one isochore (green).

into the cylinder when the air temperature is sufficient for fuel ignition. The rate at which fuel is injected is adjusted so that the ignition process takes place at constant pressure. Thus, in a Diesel engine, step DA is an isobar. The compression ratio is $r \equiv V_{\rm B}/V_{\rm D}$, and the *cutoff ratio* is $s \equiv V_{\rm A}/V_{\rm D}$. This refinement of the Otto cycle allows for higher compression ratios (of about 20) in practice, and greater engine efficiency.

For the Diesel cycle, we have, briefly,

$$\begin{aligned} W &= p_{\rm A}(V_{\rm A} - V_{\rm D}) + \frac{p_{\rm A}V_{\rm A} - p_{\rm B}V_{\rm B}}{\gamma - 1} + \frac{p_{\rm C}V_{\rm C} - p_{\rm D}V_{\rm D}}{\gamma - 1} \\ &= \frac{\gamma\, p_{\rm A}(V_{\rm A} - V_{\rm D})}{\gamma - 1} - \frac{(p_{\rm B} - p_{\rm C})V_{\rm B}}{\gamma - 1} \end{aligned} \tag{2.442}$$

and

$$Q_{\rm DA} = \frac{\gamma\, p_{\rm A}(V_{\rm A} - V_{\rm D})}{\gamma - 1} \quad . \tag{2.443}$$

To find the efficiency, we will need to eliminate $p_{\rm B}$ and $p_{\rm C}$ in favor of $p_{\rm A}$ using the adiabatic equation of state $d(pV^\gamma) = 0$. Thus,

$$p_{\rm B} = p_{\rm A} \cdot \left(\frac{V_{\rm A}}{V_{\rm B}}\right)^\gamma \quad , \quad p_{\rm C} = p_{\rm A} \cdot \left(\frac{V_{\rm D}}{V_{\rm B}}\right)^\gamma \quad , \tag{2.444}$$

where we've used $p_{\rm D} = p_{\rm A}$ and $V_{\rm C} = V_{\rm B}$. Putting it all together, the efficiency of the Diesel cycle is

$$\eta = \frac{W}{Q_{\rm DA}} = 1 - \frac{1}{\gamma}\,\frac{r^{1-\gamma}(s^\gamma - 1)}{s - 1} \quad . \tag{2.445}$$

2.15.3 The Joule-Brayton cycle

Our final example is the Joule-Brayton cycle, depicted in fig. 2.42, consisting of two adiabats and two isobars. Along the adiabats we have

$$p_2\, V_{\rm A}^\gamma = p_1\, V_{\rm D}^\gamma \quad , \quad p_2\, V_{\rm B}^\gamma = p_1\, V_{\rm C}^\gamma \quad , \tag{2.446}$$

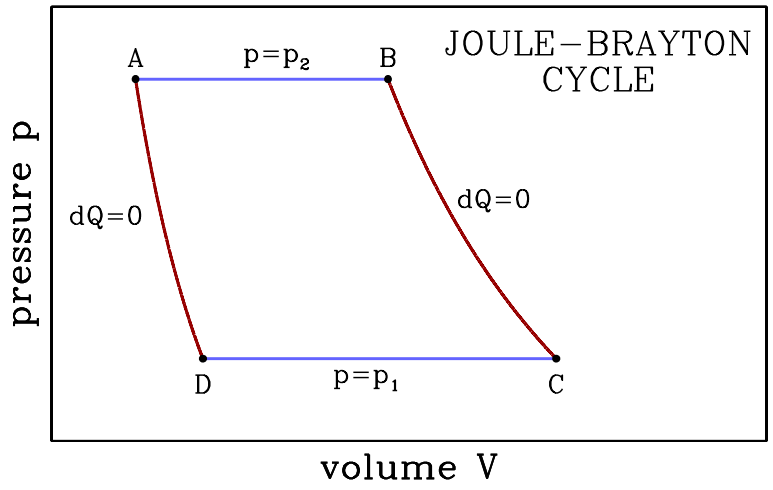


Figure 2.42: A Joule-Brayton cycle consists of two adiabats (dark red) and two isobars (light blue).

which says

$$\frac{V_{\rm D}}{V_{\rm A}} = \frac{V_{\rm C}}{V_{\rm B}} = \left(\frac{p_2}{p_1}\right)^{1/\gamma} \quad . \tag{2.447}$$

AB: This isobaric expansion at $p = p_2$ is the power stroke. We have

$$W_{\rm AB} = \int_{V_{\rm A}}^{V_{\rm B}} dV\, p_2 = p_2\,(V_{\rm B} - V_{\rm A}) \tag{2.448}$$

$$\Delta E_{\rm AB} = E_{\rm B} - E_{\rm A} = \frac{p_2\,(V_{\rm B} - V_{\rm A})}{\gamma - 1} \tag{2.449}$$

$$Q_{\rm AB} = \Delta E_{\rm AB} + W_{\rm AB} = \frac{\gamma\, p_2\,(V_{\rm B} - V_{\rm A})}{\gamma - 1} \quad . \tag{2.450}$$

BC: Adiabatic expansion; $Q_{\rm BC} = 0$ and $W_{\rm BC} = E_{\rm B} - E_{\rm C}$. The work done by the gas is

$$\begin{aligned} W_{\rm BC} &= \frac{p_2 V_{\rm B} - p_1 V_{\rm C}}{\gamma - 1} = \frac{p_2 V_{\rm B}}{\gamma - 1}\left(1 - \frac{p_1}{p_2}\cdot\frac{V_{\rm C}}{V_{\rm B}}\right) \\ &= \frac{p_2\, V_{\rm B}}{\gamma - 1}\left[1 - \left(\frac{p_1}{p_2}\right)^{1-\gamma^{-1}}\right] \quad . \end{aligned} \tag{2.451}$$

CD: Isobaric compression at $p = p_1$.

$$W_{\rm CD} = \int_{V_{\rm C}}^{V_{\rm D}} dV\, p_1 = p_1\,(V_{\rm D} - V_{\rm C}) = -p_2\,(V_{\rm B} - V_{\rm A})\left(\frac{p_1}{p_2}\right)^{1-\gamma^{-1}} \tag{2.452}$$

$$\Delta E_{\rm CD} = E_{\rm D} - E_{\rm C} = \frac{p_1\,(V_{\rm D} - V_{\rm C})}{\gamma - 1} \tag{2.453}$$

$$Q_{\rm CD} = \Delta E_{\rm CD} + W_{\rm CD} = -\frac{\gamma\, p_2}{\gamma - 1}\,(V_{\rm B} - V_{\rm A})\left(\frac{p_1}{p_2}\right)^{1-\gamma^{-1}} \quad . \tag{2.454}$$

DA: Adiabatic compression; $Q_{\rm DA} = 0$ and $W_{\rm DA} = E_{\rm D} - E_{\rm A}$. The work done by the gas is

$$\begin{aligned} W_{\rm DA} &= \frac{p_1 V_{\rm D} - p_2 V_{\rm A}}{\gamma - 1} = -\frac{p_2 V_{\rm A}}{\gamma - 1}\left(1 - \frac{p_1}{p_2}\cdot\frac{V_{\rm D}}{V_{\rm A}}\right) \\ &= -\frac{p_2\, V_{\rm A}}{\gamma - 1}\left[1 - \left(\frac{p_1}{p_2}\right)^{1-\gamma^{-1}}\right] \quad . \end{aligned} \tag{2.455}$$

The total work done per cycle is then

$$\begin{aligned} W &= W_{\rm AB} + W_{\rm BC} + W_{\rm CD} + W_{\rm DA} \\ &= \frac{\gamma\, p_2\,(V_{\rm B} - V_{\rm A})}{\gamma - 1}\left[1 - \left(\frac{p_1}{p_2}\right)^{1-\gamma^{-1}}\right] \end{aligned} \tag{2.456}$$

and the efficiency is defined to be

$$\eta \equiv \frac{W}{Q_{\rm AB}} = 1 - \left(\frac{p_1}{p_2}\right)^{1-\gamma^{-1}} \quad . \tag{2.457}$$

2.16 Appendix III: Legendre Transformations

A *strictly convex function* of a single variable $f(x)$ is one for which $f''(x) > 0$ everywhere. The *Legendre transform* of a strictly convex function $f(x)$ is a function $g(p)$ defined as follows. Let p be a real number, and consider the line $y = px$, as shown in fig. 2.43. We define the point $x(p)$ as the value of x for which the difference $F(x,p) = px - f(x)$ is greatest. Then define $g(p) = F\big(x(p), p\big)$.[35] The value $x(p)$ is unique if $f(x)$ is strictly convex, since $x(p)$ is determined by the equation

$$f'\big(x(p)\big) = p \quad . \tag{2.458}$$

Note that from $p = f'\big(x(p)\big)$ we have, according to the chain rule,

$$1 = \frac{d}{dp}\, f'\big(x(p)\big) = f''\big(x(p)\big)\, x'(p) \qquad \Longrightarrow \qquad x'(p) = \Big[f''\big(x(p)\big)\Big]^{-1} \quad . \tag{2.459}$$

[35] Note that $g(p)$ may be a negative number, if the line $y = px$ lies everywhere below $f(x)$.

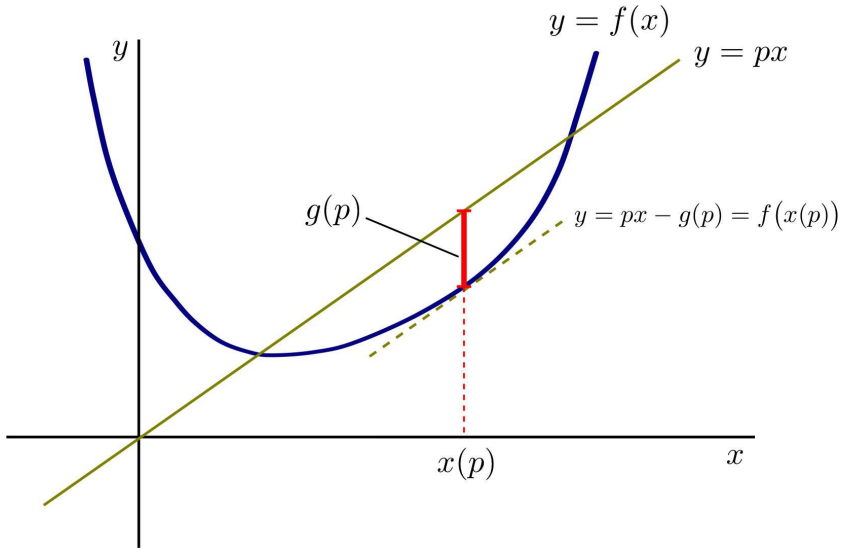


Figure 2.43: Construction for the Legendre transformation of a function $f(x)$.

From this, we can prove that $g(p)$ is itself strictly convex:

$$\begin{aligned} g'(p) &= \frac{d}{dp}\Big[p\,x(p) - f\big(x(p)\big)\Big] \\ &= p\,x'(p) + x(p) - f'\big(x(p)\big)\,x'(p) = x(p) \quad , \end{aligned} \tag{2.460}$$

hence

$$g''(p) = x'(p) = \Big[f''\big(x(p)\big)\Big]^{-1} > 0 \quad . \tag{2.461}$$

In higher dimensions, the generalization of the definition $f''(x) > 0$ is that a function $F(x_1, \ldots, x_n)$ is strictly convex if the matrix of second derivatives, called the *Hessian*,

$$H_{ij}(\boldsymbol{x}) = \frac{\partial^2 F}{\partial x_i\,\partial x_j} \tag{2.462}$$

is positive definite. That is, all the eigenvalues of $H_{ij}(\boldsymbol{x})$ must be positive for every $\boldsymbol{x}$. We then define the Legendre transform $\boldsymbol{G}(\boldsymbol{p})$ as

$$\boldsymbol{G}(\boldsymbol{p}) = \boldsymbol{p}\cdot\boldsymbol{x} - F(\boldsymbol{x}) \tag{2.463}$$

where $\boldsymbol{p} = \boldsymbol{\nabla} F$. Note that

$$dG = \boldsymbol{x}\cdot d\boldsymbol{p} + \boldsymbol{p}\cdot d\boldsymbol{x} - \boldsymbol{\nabla}F\cdot d\boldsymbol{x} = \boldsymbol{x}\cdot d\boldsymbol{p} \quad , \tag{2.464}$$

which establishes that G is a function of $\boldsymbol{p}$ and that

$$\frac{\partial G}{\partial p_j} = x_j \quad . \tag{2.465}$$

Note also that the Legendre transformation is *self-dual*, which is to say that the Legendre transform of $G(\boldsymbol{p})$ is $F(\boldsymbol{x})$: $F \to G \to F$ under successive Legendre transformations.

2.16.1 Partial Legendre transformation

We can also define a *partial Legendre transformation* as follows. Consider a function of q variables $F(\boldsymbol{x}, \boldsymbol{y})$, where $\boldsymbol{x} = \{x_1, \ldots, x_m\}$ and $\boldsymbol{y} = \{y_1, \ldots, y_n\}$, with $q = m + n$. Define $\boldsymbol{p} = \{p_1, \ldots, p_m\}$, and

$$G(\boldsymbol{p}, \boldsymbol{y}) = \boldsymbol{p} \cdot \boldsymbol{x} - F(\boldsymbol{x}, \boldsymbol{y}) \quad , \tag{2.466}$$

where

$$p_a = p_a(\boldsymbol{x}, \boldsymbol{y}) = \left(\frac{\partial F}{\partial x_a} \right)_{\boldsymbol{y}} \quad . \tag{2.467}$$

Note that we may also write

$$x_a = x_a(\boldsymbol{p}, \boldsymbol{y}) = \left(\frac{\partial G}{\partial p_a} \right)_{\boldsymbol{y}} \quad . \tag{2.468}$$

For the full Hessian of F, write

$$H = \begin{pmatrix} K & B \\ B^{\mathsf{T}} & L \end{pmatrix} \quad , \tag{2.469}$$

where

$$K_{ab} = \frac{\partial^2 F}{\partial x_a \partial x_b} \quad , \quad B_{a\nu} = \frac{\partial^2 F}{\partial x_a \partial y_\nu} \quad , \quad L_{\mu\nu} = \frac{\partial^2 F}{\partial y_\mu \partial y_\nu} \quad . \tag{2.470}$$

The variation of x^a at fixed $\boldsymbol{p}$ is then given by setting

$$0 = \left(\frac{\partial p_a}{\partial y_\nu} \right)_{\boldsymbol{p}} = K_{ab} \left(\frac{\partial x_b}{\partial y_\nu} \right)_{\boldsymbol{p}} + B_{a\nu} \quad \Rightarrow \quad \left(\frac{\partial x_a}{\partial y_\nu} \right)_{\boldsymbol{p}} = -K^{-1}_{ab} B_{b\nu} \quad . \tag{2.471}$$

Now from eqn. 2.466 we have

$$dG = x_a \, dp_a + \overbrace{p_a \, dx_a - \frac{\partial F}{\partial x_a} \, dx_a}^{\text{these cancel}} - \frac{\partial F}{\partial y_\nu} \, dy_\nu = x_a \, dp_a - \frac{\partial F}{\partial y_\nu} \, dy_\nu \quad , \tag{2.472}$$

and setting $d\boldsymbol{p} = 0$ we obtain

$$\frac{\partial G(\boldsymbol{p}, \boldsymbol{y})}{\partial y_\nu} = - \frac{\partial F(\boldsymbol{x}, \boldsymbol{y})}{\partial y_\nu} \bigg|_{\boldsymbol{x} = \boldsymbol{x}(\boldsymbol{p}, \boldsymbol{y})} \quad . \tag{2.473}$$

We then have

$$\frac{\partial^2 G}{\partial y_\mu \partial y_\nu} = - \frac{\partial^2 F}{\partial y_\mu \partial y_\nu} - \frac{\partial^2 F}{\partial x_a \partial y_\mu} \left(\frac{\partial x_a}{\partial y_\nu} \right)_{\boldsymbol{p}} \tag{2.474}$$

and thus

$$G_{\mu\nu} = -L_{\mu\nu} - B^{\mathsf{T}}_{\mu a} \left(\frac{\partial x_a}{\partial y_\nu} \right)_{\boldsymbol{p}} \quad . \tag{2.475}$$

Now invoking eqn. 2.471 we arrive at our final result relating the Hessian blocks,

$$\frac{\partial^2 G}{\partial y_\mu \partial y_\nu} = \left(B^{\mathsf{T}} K^{-1} B - L \right)_{\mu\nu} \quad . \tag{2.476}$$

Note the dimensions: $K^{m\times m}$, $L^{n\times n}$, and $B^{m\times n}$.

It is easy to see that if the full $q \times q$ Hessian matrix H_{ij} is positive definite, then any diagonal subblock such as K_{ab} or $L_{\mu\nu}$ must also be positive definite. In this case, the partial Legendre transform is convex in $\{p_1, \ldots, p_m\}$ and concave in $\{y_1, \ldots, y_n\}$.

2.17 Appendix IV: Useful Mathematical Relations

Consider a set of n independent variables $\{x_1, \ldots, x_n\}$, which can be thought of as a point in n-dimensional space. Let $\{y_1, \ldots, y_n\}$ and $\{z_1, \ldots, z_n\}$ be other choices of coordinates. Then

$$\frac{\partial x_i}{\partial z_k} = \frac{\partial x_i}{\partial y_j}\,\frac{\partial y_j}{\partial z_k} \quad . \tag{2.477}$$

Note that this entails a matrix multiplication: $A_{ik} = B_{ij}\,C_{jk}$, where $A_{ik} = \partial x_i/\partial z_k$, $B_{ij} = \partial x_i/\partial y_j$, and $C_{jk} = \partial y_j/\partial z_k$. We define the determinant

$$\det\left(\frac{\partial x_i}{\partial z_k}\right) \equiv \frac{\partial(x_1, \ldots, x_n)}{\partial(z_1, \ldots, z_n)} \quad . \tag{2.478}$$

Such a determinant is called a Jacobian. Now if $A = BC$, then $\det(A) = \det(B) \cdot \det(C)$. Thus,

$$\frac{\partial(x_1, \ldots, x_n)}{\partial(z_1, \ldots, z_n)} = \frac{\partial(x_1, \ldots, x_n)}{\partial(y_1, \ldots, y_n)} \cdot \frac{\partial(y_1, \ldots, y_n)}{\partial(z_1, \ldots, z_n)} \quad . \tag{2.479}$$

Recall also that

$$\frac{\partial x_i}{\partial x_k} = \delta_{ik} \quad . \tag{2.480}$$

Consider the case $n = 2$. We have

$$\frac{\partial(x,y)}{\partial(u,v)} = \det\begin{pmatrix} \left(\frac{\partial x}{\partial u}\right)_v & \left(\frac{\partial x}{\partial v}\right)_u \\ \left(\frac{\partial y}{\partial u}\right)_v & \left(\frac{\partial y}{\partial v}\right)_u \end{pmatrix} = \left(\frac{\partial x}{\partial u}\right)_v \left(\frac{\partial y}{\partial v}\right)_u - \left(\frac{\partial x}{\partial v}\right)_u \left(\frac{\partial y}{\partial u}\right)_v \quad . \tag{2.481}$$

We also have

$$\frac{\partial(x,y)}{\partial(u,v)} \cdot \frac{\partial(u,v)}{\partial(r,s)} = \frac{\partial(x,y)}{\partial(r,s)} \quad . \tag{2.482}$$

From this simple mathematics follows several very useful results.

1) First, write

$$\frac{\partial(x,y)}{\partial(u,v)} = \left[\frac{\partial(u,v)}{\partial(x,y)}\right]^{-1} \quad . \tag{2.483}$$

Now let $v = y$:

$$\frac{\partial(x,y)}{\partial(u,y)} = \left(\frac{\partial x}{\partial u}\right)_y = 1 \Big/ \left(\frac{\partial u}{\partial x}\right)_y \quad . \tag{2.484}$$

Thus,

$$\left(\frac{\partial x}{\partial u}\right)_y = 1 \Big/ \left(\frac{\partial u}{\partial x}\right)_y \tag{2.485}$$

2) Second, we have

$$\frac{\partial(x,y)}{\partial(u,y)} = \left(\frac{\partial x}{\partial u}\right)_y = \frac{\partial(x,y)}{\partial(x,u)} \cdot \frac{\partial(x,u)}{\partial(u,y)} = -\left(\frac{\partial y}{\partial u}\right)_x \left(\frac{\partial x}{\partial y}\right)_u \quad ,$$

which is to say

$$\left(\frac{\partial x}{\partial y}\right)_u \left(\frac{\partial y}{\partial u}\right)_x = -\left(\frac{\partial x}{\partial u}\right)_y \quad . \tag{2.486}$$

Invoking eqn. 2.485, we conclude that

$$\left(\frac{\partial x}{\partial y}\right)_u \left(\frac{\partial y}{\partial u}\right)_x \left(\frac{\partial u}{\partial x}\right)_y = -1 \quad . \tag{2.487}$$

3) Third, we have

$$\frac{\partial(x,v)}{\partial(u,v)} = \frac{\partial(x,v)}{\partial(y,v)} \cdot \frac{\partial(y,v)}{\partial(u,v)} \quad , \tag{2.488}$$

which says

$$\left(\frac{\partial x}{\partial u}\right)_v = \left(\frac{\partial x}{\partial y}\right)_v \left(\frac{\partial y}{\partial u}\right)_v \tag{2.489}$$

This is simply the chain rule of partial differentiation.

4) Fourth, we have

$$\begin{aligned} \frac{\partial(x,y)}{\partial(u,y)} &= \frac{\partial(x,y)}{\partial(u,v)} \cdot \frac{\partial(u,v)}{\partial(u,y)} \\ &= \left(\frac{\partial x}{\partial u}\right)_v \left(\frac{\partial y}{\partial v}\right)_u \left(\frac{\partial v}{\partial y}\right)_u - \left(\frac{\partial x}{\partial v}\right)_u \left(\frac{\partial y}{\partial u}\right)_v \left(\frac{\partial v}{\partial y}\right)_u \quad , \end{aligned} \tag{2.490}$$

which says

$$\left(\frac{\partial x}{\partial u}\right)_y = \left(\frac{\partial x}{\partial u}\right)_v - \left(\frac{\partial x}{\partial y}\right)_u \left(\frac{\partial y}{\partial u}\right)_v \tag{2.491}$$

5) Fifth, whenever we differentiate one extensive quantity with respect to another, holding only intensive quantities constant, the result is simply the ratio of those extensive quantities. For example,

$$\left(\frac{\partial S}{\partial V}\right)_{p,T} = \frac{S}{V} \quad . \tag{2.492}$$

The reason should be obvious. In the above example, $S(p,V,T) = V\phi(p,T)$, where ϕ is a function of the two intensive quantities p and T. Hence differentiating S with respect to V holding p and T constant is the same as dividing S by V. Note that this implies

$$\left(\frac{\partial S}{\partial V}\right)_{p,T} = \left(\frac{\partial S}{\partial V}\right)_{p,\mu} = \left(\frac{\partial S}{\partial V}\right)_{n,T} = \frac{S}{V} \quad , \tag{2.493}$$

where $n = N/V$ is the particle density.

6) Sixth, suppose we have a function $\Phi(y, v)$ and we write

$$d\Phi = x\,dy + u\,dv \quad . \tag{2.494}$$

That is,

$$x = \left(\frac{\partial \Phi}{\partial y}\right)_v \equiv \Phi_y \qquad , \qquad u = \left(\frac{\partial \Phi}{\partial v}\right)_y \equiv \Phi_v \quad . \tag{2.495}$$

Now we may write

$$dx = \Phi_{yy}\,dy + \Phi_{yv}\,dv \tag{2.496}$$

$$du = \Phi_{vy}\,dy + \Phi_{vv}\,dv \quad . \tag{2.497}$$

If we demand $dv = 0$, this yields

$$\left(\frac{\partial x}{\partial u}\right)_v = \frac{\Phi_{yy}}{\Phi_{vy}} \quad . \tag{2.498}$$

Note that $\Phi_{vy} = \Phi_{yv}$. From the equation $du = 0$ we also derive

$$\left(\frac{\partial y}{\partial v}\right)_u = -\frac{\Phi_{vv}}{\Phi_{vy}} \quad . \tag{2.499}$$

Next, we use eqn. 2.497 with $du = 0$ to eliminate dy in favor of dv, and then substitute into eqn. 2.496. This yields

$$\left(\frac{\partial x}{\partial v}\right)_u = \Phi_{yv} - \frac{\Phi_{yy}\,\Phi_{vv}}{\Phi_{vy}} \quad . \tag{2.500}$$

Finally, eqn. 2.497 with $dv = 0$ yields

$$\left(\frac{\partial y}{\partial u}\right)_v = \frac{1}{\Phi_{vy}} \quad . \tag{2.501}$$

Combining the results of eqns. 2.498, 2.499, 2.500, and 2.501, we have

$$\begin{aligned} \frac{\partial(x,y)}{\partial(u,v)} &= \left(\frac{\partial x}{\partial u}\right)_v \left(\frac{\partial y}{\partial v}\right)_u - \left(\frac{\partial x}{\partial v}\right)_u \left(\frac{\partial y}{\partial u}\right)_v \\ &= \left(\frac{\Phi_{yy}}{\Phi_{vy}}\right)\left(-\frac{\Phi_{vv}}{\Phi_{vy}}\right) - \left(\Phi_{yv} - \frac{\Phi_{yy}\,\Phi_{vv}}{\Phi_{vy}}\right)\left(\frac{1}{\Phi_{vy}}\right) = -1 \quad . \end{aligned} \tag{2.502}$$

Thus, if $\Phi = E(S, V)$, then $(x, y) = (T, S)$ and $(u, v) = (-p, V)$, we have

$$\frac{\partial(x,y)}{\partial(u,v)} = \frac{\partial(T,S)}{\partial(-p,V)} = -1 \quad . \tag{2.503}$$

Nota bene: It is important to understand what other quantities are kept constant, else problems may arise. For example, take $\Phi = G(p, N)$, whence $(x, y) = (V, p)$ and $(u, v) = (\mu, N)$, hence eqn. 2.502 yields

$$\frac{\partial(x,y)}{\partial(u,v)} = \frac{\partial(V,p)}{\partial(\mu,N)} = \frac{\partial(-p,V)}{\partial(\mu,N)} = -1 \quad . \tag{2.504}$$

But then it seems that we should have

$$\frac{\partial(T,S)}{\partial(\mu,N)} = \frac{\partial(T,S)}{\partial(-p,V)} \cdot \frac{\partial(-p,V)}{\partial(\mu,N)} = +1 \qquad \textbf{(WRONG!)}$$

when it should be -1: if $\Phi = F(T,N)$, then $(x,y) = (-S,T)$ and $(u,v) = (\mu,N)$, and again from eqn. 2.502 we have

$$\frac{\partial(x,y)}{\partial(u,v)} = \frac{\partial(-S,T)}{\partial(\mu,N)} = \frac{\partial(T,S)}{\partial(\mu,N)} = -1 \quad . \tag{2.505}$$

What has gone wrong?

The problem is that we haven't been consistent in what is being held constant. In eqn. 2.503 we are implicitly taking $dN = 0$ since $(y,v) = (S,V)$ and $E = E(S,V,N)$. In eqn. 2.504 we take $dT = 0$ since $(y,v) = (p,N)$ and $G = G(T,p,N)$. And in eqn. 2.505 we take $dV = 0$ since $(y,v) = (T,N)$ and $F = F(T,p,N)$. Thus a naïve and careless application of the chain rule for determinants yields the wrong result.

Let's be more careful. Applying the same derivation to $dE = x\,dy + u\,dv + r\,ds$ and holding s constant, we conclude

$$\frac{\partial(x,y,s)}{\partial(u,v,s)} = \left(\frac{\partial x}{\partial u}\right)_{v,s}\left(\frac{\partial y}{\partial v}\right)_{u,s} - \left(\frac{\partial x}{\partial v}\right)_{u,s}\left(\frac{\partial y}{\partial u}\right)_{v,s} = -1 \quad . \tag{2.506}$$

Thus, if

$$dE = T\,dS + y\,dX + \mu\,dN \quad , \tag{2.507}$$

where $(y,X) = (-p,V)$ or (H^α, M^α) or (E^α, P^α), the appropriate thermodynamic relations are

$$\begin{aligned}
\frac{\partial(T,S,N)}{\partial(y,X,N)} &= -1 & \qquad \frac{\partial(T,S,\mu)}{\partial(y,X,\mu)} &= -1 \\
\frac{\partial(\mu,N,X)}{\partial(T,S,X)} &= -1 & \qquad \frac{\partial(\mu,N,y)}{\partial(T,S,y)} &= -1 \\
\frac{\partial(y,X,S)}{\partial(\mu,N,S)} &= -1 & \qquad \frac{\partial(y,X,T)}{\partial(\mu,N,T)} &= -1
\end{aligned} \tag{2.508}$$

For example,

$$\frac{\partial(T,S,N)}{\partial(-p,V,N)} = \frac{\partial(-p,V,S)}{\partial(\mu,N,S)} = \frac{\partial(\mu,N,V)}{\partial(T,S,V)} = -1 \tag{2.509}$$

and

$$\frac{\partial(T,S,\mu)}{\partial(-p,V,\mu)} = \frac{\partial(-p,V,T)}{\partial(\mu,N,T)} = \frac{\partial(\mu,N,-p)}{\partial(T,S,-p)} = -1 \quad . \tag{2.510}$$

If we are careful, then the results in eq. 2.508 can be quite handy, especially when used in conjunction with eqn. 2.479. For example, we have

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \frac{\partial(T,S,N)}{\partial(T,V,N)} = \overbrace{\frac{\partial(T,S,N)}{\partial(p,V,N)}}^{=1} \cdot \frac{\partial(p,V,N)}{\partial(T,V,N)} = \left(\frac{\partial p}{\partial T}\right)_{V,N} \quad , \tag{2.511}$$

which is one of the Maxwell relations derived from the exactness of $dF(T,V,N)$. Some other examples include

$$\left(\frac{\partial V}{\partial S}\right)_{p,N} = \frac{\partial(V,p,N)}{\partial(S,p,N)} = \overbrace{\frac{\partial(V,p,N)}{\partial(S,T,N)}}^{=1} \cdot \frac{\partial(S,T,N)}{\partial(S,p,N)} = \left(\frac{\partial T}{\partial p}\right)_{S,N} \tag{2.512}$$

$$\left(\frac{\partial S}{\partial N}\right)_{T,p} = \frac{\partial(S,T,p)}{\partial(N,T,p)} = \overbrace{\frac{\partial(S,T,p)}{\partial(\mu,N,p)}}^{=1} \cdot \frac{\partial(\mu,N,p)}{\partial(N,T,p)} = -\left(\frac{\partial \mu}{\partial T}\right)_{p,N} \quad , \tag{2.513}$$

which are Maxwell relations deriving from $dH(S,p,N)$ and $dG(T,p,N)$, respectively. Note that due to the alternating nature of the determinant – it is antisymmetric under interchange of any two rows or columns – we have

$$\frac{\partial(x,y,z)}{\partial(u,v,w)} = -\frac{\partial(y,x,z)}{\partial(u,v,w)} = \frac{\partial(y,x,z)}{\partial(w,v,u)} = \ldots \quad . \tag{2.514}$$

In general, it is usually advisable to eliminate S from a Jacobian. If we have a Jacobian involving T, S, and N, we can write

$$\frac{\partial(T,S,N)}{\partial(\bullet\,,\bullet\,,N)} = \frac{\partial(T,S,N)}{\partial(p,V,N)}\,\frac{\partial(p,V,N)}{\partial(\bullet\,,\bullet\,,N)} = \frac{\partial(p,V,N)}{\partial(\bullet\,,\bullet\,,N)} \quad , \tag{2.515}$$

where each $\bullet$ is a distinct arbitrary state variable other than N.

If our Jacobian involves S, V, and N, we write

$$\frac{\partial(S,V,N)}{\partial(\bullet\,,\bullet\,,N)} = \frac{\partial(S,V,N)}{\partial(T,V,N)} \cdot \frac{\partial(T,V,N)}{\partial(\bullet\,,\bullet\,,N)} = \frac{C_V}{T} \cdot \frac{\partial(T,V,N)}{\partial(\bullet\,,\bullet\,,N)} \quad . \tag{2.516}$$

If our Jacobian involves S, p, and N, we write

$$\frac{\partial(S,p,N)}{\partial(\bullet\,,\bullet\,,N)} = \frac{\partial(S,p,N)}{\partial(T,p,N)} \cdot \frac{\partial(T,p,N)}{\partial(\bullet\,,\bullet\,,N)} = \frac{C_p}{T} \cdot \frac{\partial(T,p,N)}{\partial(\bullet\,,\bullet\,,N)} \quad . \tag{2.517}$$

For example,

$$\left(\frac{\partial T}{\partial p}\right)_{S,N} = \frac{\partial(T,S,N)}{\partial(p,S,N)} = \overbrace{\frac{\partial(T,S,N)}{\partial(p,V,N)}}^{=1} \cdot \frac{\partial(p,V,N)}{\partial(p,T,N)} \cdot \frac{\partial(p,T,N)}{\partial(p,S,N)} = \frac{T}{C_p}\left(\frac{\partial V}{\partial T}\right)_{p,N} \tag{2.518}$$

$$\left(\frac{\partial V}{\partial p}\right)_{S,N} = \frac{\partial(V,S,N)}{\partial(p,S,N)} = \frac{\partial(V,S,N)}{\partial(V,T,N)} \cdot \frac{\partial(V,T,N)}{\partial(p,T,N)} \cdot \frac{\partial(p,T,N)}{\partial(p,S,N)} = \frac{C_V}{C_p}\left(\frac{\partial V}{\partial p}\right)_{T,N} \quad . \tag{2.519}$$

With $\kappa \equiv -\frac{1}{V}\frac{\partial V}{\partial p}$ the compressibility, we see that the second of these equations says $\kappa_T\, c_V = \kappa_S\, c_p$, relating the isothermal and adiabatic compressibilities and the molar heat capacities at constant volume and constant pressure. This relation was previously established in eqn. 2.266.