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Statistical Mechanics, Spring 2021

Lecture 8: Free energy

1 Introduction

Using our various ensembles, we were led to a rather simple differential relation between energy and other state variables, Eq. (55) of Lecture 7:

$$dE = TdS - PdV + \mu dN \tag{1}$$

The terms on the right are different ways the energy can change: the first term is heat, since $dS = \frac{dQ}{T}$, the second term is work from expanding volume, the third term is the energy associated with bond formation or particle creation.

Holding any two of the four differentials fixed we can derive from this equation lots of other formulas

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

and so on. Some of these are more useful than others.

The way to think about these differential relations is that they relate small changes of E, S, V and N, with T, P and μ giving the relative size relating the small changes. So the functions depend only on the other differential variables.

$$E = E(S,V,N), \qquad S = S(E,V,N), \qquad V = V(E,S,N), \qquad N = N(E,S,V) \tag{3}$$

The variables T, P, μ are derived quantities. They are calculated by taking partial derivatives with respect to the independent variables. That is, if one of the functional forms is known, such as $S(E,V,N)$, we can find T, P and μ by taking derivatives.

Since partial derivatives commute, we can derive some additional relations amount derivatives:

$$\left(\frac{\partial T}{\partial V}\right)_{S,N} = \left(\frac{\partial}{\partial V}\left(\frac{\partial E}{\partial S}\right)_{V,N}\right)_{S,N} = \left(\frac{\partial}{\partial S}\left(\frac{\partial E}{\partial V}\right)_{S,N}\right)_{V,N} = -\left(\frac{\partial P}{\partial S}\right)_{V,N} \tag{4}$$

and so on. These type of relations among derivatives are known as **Maxwell relations**.

Keep in mind that the general relations amount E, S, V, N, T, P, μ hold for *any* system. The first 3 equations in Eq. (2) are the *definitions* of T, μ and P. The others follow mathematically from these using elementary multivariate calculus. Starting with the specification of a system in any ensemble (micro, canonical, or grand canonical), we can compute these quantities and the relations will hold. We often use monatomic ideal gases to check these general relations. For example,, the entropy of a monatomic ideal gas is

$$S(E,V,N) = Nk_B\left[\ln\frac{V}{N} + \frac{3}{2}\ln\left(\frac{4\pi mE}{3Nh^2}\right) + \frac{5}{2}\right] \tag{5}$$

Then

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{3}{2}\frac{Nk_B}{E} \quad \Longrightarrow \quad E = \frac{3}{2}Nk_BT \tag{6}$$

which is the statement $\frac{3}{2}Nk_BT$, is the average kinetic energy of a gas. Another one is,

$$P = T\left(\frac{\partial S}{\partial V}\right)_{E,N} = T\frac{Nk_B}{V} \quad \Longrightarrow \quad PV = Nk_BT \tag{7}$$

which is the ideal gas law, and so on.

When we have a function like $S(V,E,N)$, we can easily see how the system responds when we change V,E and N. In physical situations, we are often much more interested in knowing how our system responds to changes in temperature (when we heat it) or pressure (when we compress it), or, for chemical reactions in particular, how to characterize equilibrium properties of a system when T and P are held fixed. So we would like the system to be described by functions that depend explicitly on T and P rather than E and V. In this lecture, we construct new variables (free energies) that depend on T and P. The four new potentials we introduce are

$$\textbf{Helmoltz free energy}: \quad F \equiv E - TS \tag{8}$$

$$\textbf{Enthalpy}: \quad H \equiv E + PV \tag{9}$$

$$\textbf{Gibbs free energy}: \quad G \equiv E + PV - TS \tag{10}$$

$$\textbf{Grand free energy}: \quad \Phi \equiv E - TS - \mu N \tag{11}$$

These are general definitions of these new variables, holding for arbitrary systems. We will work through these, constructing them, showing what the depend on, and then exploring their physical significance.

As a warning, this business of dependent and independent variables is going to be one of the most confusing and infuriating things in the course. Unfortunately, it is essential to understanding thermodynamics so there's no getting around it. We'll try to be as clear about what is going on as possible.

As another piece of advice going forward: sequester in your mind all the complicated subtleties with entropy (ergodicity, Boltzmann's H theorem, Lodschmidt's paradox, Landauer's principle, etc.). If you really reach down deep to understand the foundations of the second law, all these things are important. However to *use* statistical mechanics, and thermodynamics, in physics, chemistry, astronomy and so on, we define systems based on macroscopic quantities (P,V,N,T, ...), entropy is extensive ($S_{\text{tot}} = S_1 + S_2$), the second law holds without subtlety ($\Delta S_{\text{tot}} \geqslant 0$), and μ, T and P are constant for systems in equilibrium.

2 Euler identity

Before getting started with all the new potentials, there is actually a very nice relation we can derive among all the different interdependent variables using only Eq. (1) and the fact that entropy is extensive.

From Eq. (1) we see that $S = S(E,V,N)$ (which we already knew since that's how we set up the microcanonical ensemble in the beginning). E,V,N and S are all extensive quantities. When we double the size of a system, they all double. This is in contrast to P, μ and T which are intensive quantities. When we double the system, they do not change.

It's actually very hard to make an extensive function. Any extensive function $f(x)$ must satisfy $f(cx) = cf(x)$ for any c. Differentiating with respect to c gives

$$x f'(cx) = f(x) \tag{12}$$

This holds for any c, so we can set $c = 1$. The solution to this differential equation is then $f(x) = ax$ for some a. That is, f must be a linear function of its argument to be extensive.

Now let's generalize to a function of multiple variables. Extensivity requires

$$S(cE, cV, cN) = cS(E,V,N) \tag{13}$$

Differentiating both sides with respect to c gives

$$\left(\frac{\partial S}{\partial cE}\right)_{V,N} \frac{\partial cE}{\partial c} + \left(\frac{\partial S}{\partial cV}\right)_{E,N} \frac{\partial cV}{\partial c} + \left(\frac{\partial S}{\partial cN}\right)_{V,E} \frac{\partial cN}{\partial c} = S(E,V,N) \tag{14}$$

which simplifies to

$$S = \left(\frac{\partial S(cE,cV,cN)}{\partial cE}\right)_{V,N} E + \left(\frac{\partial S(cE,cV,cN)}{\partial cV}\right)_{E,N} V + \left(\frac{\partial S(cE,cV,cN)}{\partial cN}\right)_{V,E} N \tag{15}$$

$$= \frac{E}{T} + \frac{P}{T} V - \frac{\mu}{T} N \tag{16}$$

or equivalently

$$\boxed{E = TS - PV + \mu N} \tag{17}$$

This is known as the **Euler equation**. You can check it yourself for a monatomic ideal gas.

A related result comes from taking the total derivative of both sides

$$dE = d(\mathrm{TS}) - d(PV) + d(\mu N) = TdS + SdT - VdP - PdV + \mu dN + Nd\mu \tag{18}$$

Subtracting Eq. (1) we get

$$SdT - VdP + Nd\mu = 0 \tag{19}$$

This is called the **Gibbs-Duhem equation**. It says that T, P and μ are not independent – changing T and P constrains exactly the way μ changes. The Gibbs-Duhem equation generates a whole new set of partial derivative identies such as

$$\left(\frac{dP}{dT}\right)_{\mu} = \frac{S}{V}, \quad \left(\frac{dT}{d\mu}\right)_{P} = -\frac{N}{S} \tag{20}$$

and so on.

The Euler equation at the Gibbs-Duhem equation hold for almost all statistical mechanical systems. Keep in mind however that the extensivity of entropy is not guaranteed by definition, and in some situations, where there are long-range interactions like gravity, as in stars, entropy is not extensive. Indeed, famously, for a black hole, entropy scales as the *area* of the black hole's event horizon, not the volume of the hole. That being said, for the vast majority of statistical mechanical systems we will consider, the Euler equation holds. To be safe, we will avoid using the Euler equation, but rather check that it holds in situations where entropy is indeed extensive.

3 Helmholtz Free Energy

We define the **Helmholtz free energy** as

$$F \equiv E - TS \tag{21}$$

Free energy is a concept particularly useful at constant temperature.

We can take the differential of F:

$$dF = dE - TdS - SdT = -PdV + \mu dN - SdT \tag{22}$$

We used $d(TS) = TdS + SdT$, which follows from the chain rule, in the first step and Eq. (1) in the second. Note that the dS has dropped out. We can then the read off what F naturally depends on from the differentials in Eq. (22):

$$F = F(V, N, T) \tag{23}$$

This generates a whole new set of Maxwell relations, by picking two terms in Eq. (22):

$$\left(\frac{\partial F}{\partial V}\right)_{N,T} = -P, \quad \left(\frac{\partial F}{\partial N}\right)_{V,T} = \mu, \quad \left(\frac{\partial F}{\partial T}\right)_{V,N} = -S, \quad \left(\frac{\partial T}{\partial V}\right)_{F,N} = -\frac{P}{S} \tag{24}$$

and so on.

It is perhaps also worth pointing out to the mathematically-oriented crowd that the operation of replacing the dependent variable S in $E(S, V, N)$ with a new dependent variable given by a derivative, $T = \frac{\partial E}{\partial S}$, is known as a **Legendre transform**. Another example of a Legendre transform is going from a Lagrangian $L(\dot{q}, q)$ that depends on velocity $\dot{q}$ to a Hamiltonian $H(p, q)$ that depends on momentum $p = \frac{\partial L}{\partial \dot{q}}$. The Hamiltonian does not depend on $\dot{q}$ just as F does not depend on S. If you're not excited by the mathematics of it, the fact that we call it a Legendre transform is of no consequence. All the physics you need comes from the definition $F = E - TS$.

Before continuing, let me try to address a common pitfall. You might ask why is there no dE in Eq. (22)? Similarly, you could ask why is there no dT in Eq. (1)? The answer is that the non-trivial content in Eq. (1) is precisely that there is no dT (and no $d\mu$ or dP either). Of course T does vary, so if we have a nonzero dN, dV and dS then dT is probably nonzero as well. The point is that dT is not an *independent* variation. Eq. (1) says that we don't need to know what dT is to compute dE, we just need dS, dV and dN. Similarly, the content of Eq. (22) is that we don't need to know dE or dS, it is enough to know dV, dN and dT. E is a dependent variable in Eq. (22), so its variation is determined by the variation of the other, independent variables. Of course, we can always change variables and write $F(P,\mu,E)$ or whatever we want. However, there are not simple formulas for $\left(\frac{\partial F}{\partial P}\right)_{\mu,E}$ so writing F this way is not useful; it does not lead to any sort of simplification.

3.1 Free energy for work

The Helmholtz free energy is one of the most useful quantities in thermodynamics. Its usefulness stems from the fact that dV, dN and dT are readily measurable. This in contrast to $E(S,V,N)$ which depends on entropy that is hard to measure and in contrast to $S(E,V,N)$ which depends on energy that is hard to measure. Helmholtz free energy is particularly powerful for systems at constant temperature where $dF = dE - TdS$. In previous courses you have studied mechanical systems using energy. Mechanical systems all fixed degrees of freedom, so $S=0$ and $F=E$. Free energy is a generalization of energy whose importance is revealed by working at finite T.

Consider an isolated system in volume V kept at constant T by being in contact with a heat bath. Imgine that the system starts in some state at V and T and ends at the same V and T. We do not need to know anything about what happens between start and end other than that the only interaction with the surroundings is through heat exchange. We would like to know what is the maximum amount of work W the system can do in this situation? In general, energy is conserved, so we know $W + \Delta E_{\text{system}} - Q = 0$ where Q is the heat drawn in from the heat bath. The change in entropy of the bath is $\Delta S_{\text{bath}} = -\frac{Q}{T}$. The work causes no change in entropy, so by the second law of thermodynamics, $\Delta S_{\text{system}} \geqslant \frac{Q}{T}$, with the equality holding only if the transformation of the system is reversible. Then the free energy change is

$$\Delta F_{\text{system}} = \Delta E_{\text{system}} - T\Delta S_{\text{system}} \leqslant (-W + Q) - T\frac{Q}{T} = -W \tag{25}$$

That is,

$$W \leqslant -\Delta F_{\text{system}} \tag{26}$$

where the inequality becomes an equality if and only if the transformation is done reversibly. So the free energy of the system is depleted to do the work. This is why free energy is called free: it is the energy available to do work. In an insulated system (not heat exchange), the energy of the system is used for work, but in an isothermal system, it is the free energy that is used for work.

Note that it was important that the system be kept at constant volume. If the volume were to change, it would have to do work on the surrounding heat bath. Such work would be immediately dissipated as heat, causing an additional entropy increase. We will consider the more physically common situation of constant pressure transformation in Section 5.

For another perspective, consider the case where no work is done, or where work is not relevant, such as when gases mix together, or some chemical reactions occur, or a system settles down after some perturbation. When $W=0$, we get from Eq. (26) that $\Delta F_{\text{system}} \leqslant 0$. Thus, in a system kept at constant temperature and volume, interacting with the surroundings only through an exchange of heat (i.e. no work), the Helmholtz free energy never increases. As the system settles down towards equilibrium, F will decrease until equilibrium is reached when it stops decreasing (if it could decrease more by a fluctuation, it would, and then it could never go up again). Therefore, in an isolated system kept at constant temperature and volume, the equilibrium is the state of minimum Helmholtz free energy.

To be extra clear, let us emphasize that free energy refers to the *free energy of the system only*, $F = F_{\text{system}}$. So to find the equilibrium state we minimize the free energy of the system, ignoring the heat bath. Indeed, this is why free energy is powerful: it lets us talk about the system alone.

For a concrete example, consider a system of two gases separated by a partition, initially with different pressures P_1 and P_2 and different volumes V_1 and V_2 with $V_1+V_2=V$, in thermal contact with a heat bath. Then, since $F=F(T,N,V)$ and T and N are fixed, the minimization condition is

$$0=dF=\left(\frac{\partial F}{\partial V_1}\right)dV_1+\left(\frac{\partial F}{\partial V_2}\right)dV_2=-P_1dV_1-P_2d(V-V_1)=(P_2-P_1)dV_1 \tag{27}$$

Thus the pressures are equal at equilibrium – if $P_1\neq P_2$ then changing V would lower F. Of course, we knew this already; previously, we derived the pressure equality from maximization of the total entropy at constant energy. Here we are deriving it from minimization of free energy of the system at constant temperature. The two are equivalent. Indeed, the second law of thermodynamics is equivalent to the minimization of free energy. In general however, it is much easier to deal with systems at constant temperature than at constant entropy, and to minimize the free energy of the system rather than to maximize the *total* entropy.

In summary,

- **Free energy is to a constant T system what E is to a mechanical system.**
- **Helmholtz free energy is the available energy to do work at constant T and V.**
- **In a system kept at constant T and V, interacting with the surroundings only through an exchange of heat (i.e. no work), the Helmholtz free energy never increases.**
- **In an isolated system at constant T and V, Helmholtz free energy is minimized in equilibrium**.
- **Free energy refers to the free energy *of the system only* $F=F_{\text{system}}$.**

Another important point to keep in mind is that free energy, like entropy, is a property of the ensemble. You cannot talk about the free energy or entropy of an individual microstate.

3.2 Free energy and the partition function

Next, consider how to compute free energy from the partition function in the canonical ensemble. Recall that in the canonical ensemble, $S=\frac{\langle E\rangle}{T}+k_B\ln Z$. So for an isolated system where $\langle E\rangle=E$ we immediately get that

$$\boxed{F=-k_BT\ln Z} \tag{28}$$

So the free energy *is* (- k_BT times the logarithm of) the partition function. It therefore carries all that useful information about the spectrum that the partition function has – the partition function and free energy are both very powerful. But it is the same power, since they are the same function. Equivalently, we can write Eq. (28) is

$$e^{-\beta F}=Z=\sum e^{-\beta E} \tag{29}$$

which shows that the free energy is the same as the energy if there is only one microstate.

For a monoatomic ideal gas recall that

$$Z=e^N\left(\frac{V}{N}\right)^N\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{3}{2}N} \tag{30}$$

So

$$F=-k_BT\ln Z=-Nk_BT\left[\ln\frac{V}{N}+\frac{3}{2}\ln\left(\frac{2\pi mk_BT}{h^2}\right)+1\right] \tag{31}$$

As a check, we note that

$$\left(\frac{\partial F}{\partial T}\right)_{V,N}=-Nk_B\left[\ln\frac{V}{N}+\frac{3}{2}\ln\left(\frac{2\pi mk_BT}{h^2}\right)+\frac{5}{2}\right]=-S \tag{32}$$

which, using that $E=\frac{3}{2}Nk_BT$ for a monatomic ideal gas, agrees with Eq. (5). Also,

$$P=-\left(\frac{\partial F}{\partial V}\right)_{T,N}=\frac{Nk_BT}{V} \tag{33}$$

in agreement with the ideal gas law.

3.3 Spring and gas

To build some more intuition for free energy, let's consider some examples. First, think about the free expansion of a gas from $V_1\to V_2$. No work is done in free expansion. The distribution of molecular speeds is the same, they just have more room to move around in, so the internal energy of the gas doesn't change either, $\Delta E=0$. The entropy change is $\Delta S=Nk_B\ln\frac{V_2}{V_1}$, as we saw in the discussion entropy of mixing. So the change in free energy is

$$\Delta F=\Delta E-T\Delta S=-Nk_BT\ln\frac{V_2}{V_1} \tag{34}$$

In this case, the transition is completely driven by entropic considerations.

Now consider a piston on a spring, with force constant k, immersed in a heat bath (e.g. freely moving in air at room temperature). The spring only has 1 degree of freedom, the position of the piston. Let x be the displacement of the piston from its equilibrium position. Its energy is

$$E(x,\dot{x})=\frac{1}{2}m\dot{x}^2+\frac{1}{2}kx^2 \tag{35}$$

The first term is kinetic energy, the second is potential energy. The entropy of the spring is zero and doesn't change as the spring moves. As the spring moves the piston, it dissipates energy into the bath. Note however that it does no *work* on the bath: all the energy transferred goes to heating up the bath; there is no sense in which the energy transferred is useful in any sense, so it cannot be doing work. Thus this system qualifies for our general results about F decreasing. Since $S=0$ for the piston+spring system, $F=E$. So minimizing F just corresponds to minimizing E. This free energy is minimized for $x=\dot{x}=0$, the equilibrium position of the spring. Alternatively, we could define the system as the spring plus the heat bath. Then, $\Delta E=0$ so $\Delta F=-T\Delta S_{\text{bath}}=-Q$. Thus free energy is minimized when the maximum amount of heat is transferred to the bath, i.e. the entire energy of the spring.

Now let's put the spring and the gas together. We'll start the gas off at volume V_1 and the spring at $x=0$:

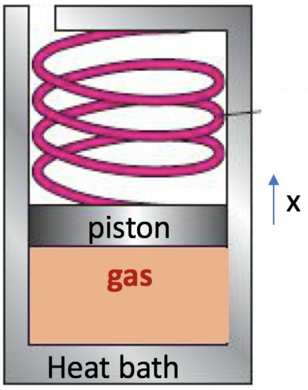


Figure 1. Spring-loaded piston against gas in a heat bath

We define the system as the piston+gas, and call the bath the surroundings. What is the equilibrium state?

To find the equilibrium, we want the free energy to be stationary when we vary x, so we need

$$\frac{\partial F}{\partial x} = \frac{\partial E}{\partial x} - T\frac{\partial S}{\partial x} \tag{36}$$

As the gas does work on the spring, it pulls heat in from the bath to stay at constant temperature. Since T is constant, the energy of the gas does not change. Thus, the energy in the gas does not depend on x. So the energy change of the system $\frac{\partial E}{\partial x}$ comes only from the spring, where we get $\frac{\partial E}{\partial x} = \mathcal{F}_{\text{piston}} = -kx$. We use the curly $\mathcal{F}$ for force to distinguish it from free energy. $\mathcal{F}_{\text{piston}}$ is the force acting on the gas by the piston. The piston doesn't have any entropy, so $\frac{\partial S}{\partial x}$ comes entirely from the gas. Now, the volume of the gas is $V = V_1 + Ax$ where A is the area of the piston. So

$$\frac{\partial S}{\partial x} = \frac{\partial S}{\partial V}\frac{\partial V}{\partial x} = \frac{P}{T}A = \frac{\mathcal{F}_{\text{gas}}}{T} \tag{37}$$

In the last step we used that pressure times area is force. So Eq. (36) becomes

$$\frac{\partial F}{\partial x} = \mathcal{F}_{\text{piston}} - \mathcal{F}_{\text{gas}} \tag{38}$$

Setting the variation of the free energy to zero, $\frac{\partial F}{\partial x} = 0$, implies $\mathcal{F}_{\text{piston}} = \mathcal{F}_{\text{gas}}$. This of course makes complete sense – we can compute the equilibrium point of the spring by demanding that the forces are equal, or we could find the equilibrium by minimizing the free energy. The result is the same.

3.4 Energy (non)-minimization

It is common lore to think of energy being minimized by physical systems: a ball rolls down to the bottom of a hill and stays there. But energy is conserved, so where does this common sense lore come from? It comes from free energy! All those systems in which energy is minimized are really minimizing free energy. You may never have thought about the gas in air surrounding the ball, but it it weren't for the gas, or the molecules in the dirt that can heat up due to friction, the ball would just roll right back up the hill.

The gas-spring example hopefully illustrated the point that there is no tendency to minimize energy. Total energy is conserved, in spontaneous motion, adiabatic motion, or whatever. The energy E in the definition $F = E - TS$ is not the total energy but rather the energy of the system. We assume the system is in thermal equilibrium, so energy in the form of heat can leave the system into the surroundings, or enter the system from the surroundings. Thus ΔE may not be zero. But the energy of system itself does not tend towards a minimum.

The tendency to minimize free energy is entirely because of a tendency to maximize entropy. This is clearest if we write

$$\Delta F = -T\left[\underbrace{\Delta S}_{\Delta S_{\text{sys}}} + \underbrace{\left(-\frac{\Delta E}{T}\right)}_{\Delta S_{\text{surr}}}\right] \tag{39}$$

The ΔS term is the entropy change of the system. The second term $\frac{\Delta E}{T} = \frac{Q}{T}$ is the entropy change of the surroundings. Their total is maximized, so entropy is maximized, and free energy is minimized. When we think of a spring with friction slowly stopping, we think it is minimizing energy. Indeed, it is minimizing energy, but that is because it is maximizing $-\frac{E}{T} = S$.

In summary, energy minimization is really free energy minimization, which really is entropy maximization.

4 Enthalpy

We use the symbol H for **enthalpy**. It is defined as

$$H \equiv E + PV \tag{40}$$

So, using Eq. (1),

$$dH = dE + PdV + VdP = TdS + VdP + \mu dN \tag{41}$$

Thus,

$$\left(\frac{\partial H}{\partial S}\right)_{P,N} = T, \qquad \left(\frac{\partial H}{\partial P}\right)_{S,N} = V, \qquad \left(\frac{\partial H}{\partial N}\right)_{P,S} = \mu \tag{42}$$

Enthalpy is a concept useful at constant pressure. It is a function $H = H(S, P, N)$.

Recall that we had two heat capacities related to how much temperature rises when heat dQ is put in at constant V or constant P

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V, \quad C_P = \left(\frac{\partial Q}{\partial T}\right)_P \tag{43}$$

For constant V, no work is done, since $W = PdV$. So $C_V = \left(\frac{\partial E}{\partial T}\right)_V$. For constant P, the gas has to expand when heat is absorbed to keep the pressure constant, so work is done and the energy goes down. The total energy change is $\Delta E = Q - P\Delta V$. In other words, $\Delta H = Q$. Thus,

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \tag{44}$$

Thus enthalpy plays the role at constant pressure that energy does at constant volume.

For a monatomic ideal gas, since $PV = Nk_BT$ and $E = \frac{3}{2}Nk_BT$ we get immediately that

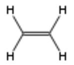
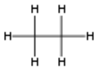
$$H = E + PV = \frac{5}{2}Nk_BT \tag{45}$$

so, from Eq. (44) $C_P = \frac{5}{2}Nk_B$ in agreement with what we found in Lecture 5.

4.1 Enthalpy of chemical bonds

Enthalpy is especially useful in chemistry, where pressure is nearly always constant but volume is not under control. For example, when you open the door to your room, the volume of the air changes, but the pressure is the same. Chemicals in a solution are also at constant pressure, as are biological reactions in cells. When you mix two solutions, the volume accessible to each changes, but the pressure is the same.

Since chemistry (and biology) takes place at constant pressure and temperature, when a chemical reaction occurs the heat released is $Q = \Delta H$. Thus when you measure the heat released or absorbed in a reaction, you are measuring the enthalpy.

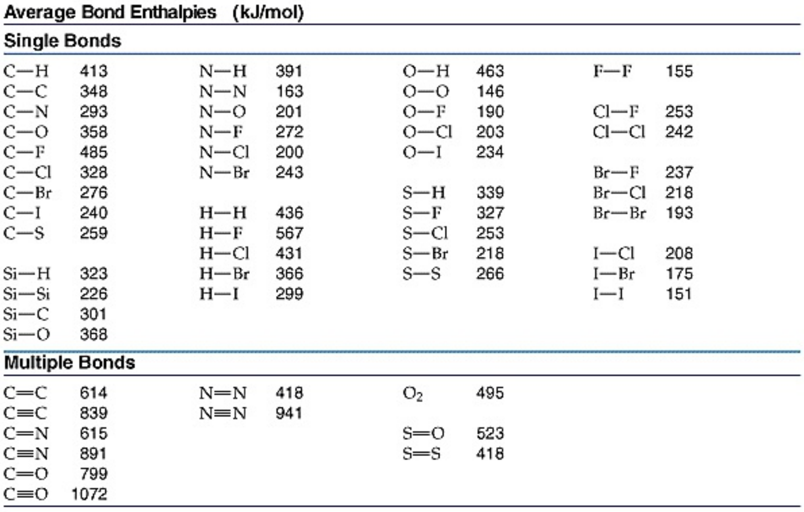
There are different ways to compute the enthalpy of a reaction, to different degrees of approximation. Consider for example the hydrogenation of ethene= (C_2H_4)=  into ethane (C_2H_6)=  :

$$H_2 + C_2H_4 \rightarrow C_2H_6 \tag{46}$$

First of all, you can just look up the enthalpy for this reaction. That is called the **standard enthalpy of reaction**, where standard means under some reference conditions, like $298K$ and 1 atm. For this reaction, we can look up at the reaction enthalpy is $\Delta_r H^\circ = -136.3 \pm 0.3\,\frac{\text{kJ}}{\text{mol}}$. The enthalpy decreases, so the reaction is exothermic: heat is released.

If we don't have the reaction enthalpy handy, we can compute the enthalpy change by taking the differences of the enthalpies of the products and the reactants. So in this case, we look up that the **enthalpy of formation** of each. The enthalpy of formation is the enthalpy change in forming something from its constituent atoms (C, S, Si) or diatomic molecules (H_2,O_2,N_2,F_2). So the enthalpy of formation of C or H_2 is 0, by definition. The enthalpy of formation for C_2H_4 is $\Delta_f H^\circ = 52.4 \pm 0.5\frac{\text{kJ}}{\text{mol}}$ and for C_2H_6 is $\Delta_f H^\circ = -84 \pm 0.4\frac{\text{kJ}}{\text{mol}}$. It takes energy to make ethane, but energy is relaeased when enthane is formed. Combining these, the enthalpy of the reaction is $\Delta_r H^\circ = -84\frac{\text{kJ}}{\text{mol}} - 52.4\frac{\text{kJ}}{\text{mol}} = -136.4\frac{\text{kJ}}{\text{mol}}$ in agreement with the directly measured enthalpy of reaction. That we can add and subtract enthalpies to get the reaction enthalpy is known as **Hess's law**. There are lots of laws in chemistry.

If we don't have the enthalpy's of formation handy, our last resort is to compute the enthalpy change ourselves by adding up the enthalpy of each bond. There are only a finite number of relevant bonds for organic chemistry, so we can just make a table of them:



Average Bond Enthalpies (kJ/mol)

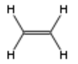
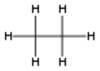
Single Bonds

C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C—N	293	N—O	201	O—F	190	Cl—F	253
C—O	358	N—F	272	O—Cl	203	Cl—Cl	242
C—F	485	N—Cl	200	O—I	234		
C—Cl	328	N—Br	243			Br—F	237
C—Br	276			S—H	339	Br—Cl	218
C—I	240	H—H	436	S—F	327	Br—Br	193
C—S	259	H—F	567	S—Cl	253		
		H—Cl	431	S—Br	218	I—Cl	208
Si—H	323	H—Br	366	S—S	266	I—Br	175
Si—Si	226	H—I	299			I—I	151
Si—C	301						
Si—O	368						

Multiple Bonds

C=C	614	N=N	418	O_2	495
C≡C	839	N≡N	941		
C=N	615			S=O	523
C≡N	891			S=S	418
C=O	799				
C≡O	1072				

Figure 2. Average enthalpies of common covalent bolds. Numbers are listed as positive, as enthalpies required to break the bonds.

So C_2H_4=  has one $C=C$ double bond, $H_b=-614\frac{\text{kJ}}{\text{mol}}$ and 4 CH bonds each with $H_b=-413\frac{\text{kJ}}{\text{mol}}$ giving it an enthalpy of $H_{C_2H_4}=-2266\frac{\text{kJ}}{\text{mol}}$. $C_2H_6=$  has 6 CH bonds and one C-C single bond, giving it $H_{C_2H_6}=-2826\frac{\text{kJ}}{\text{mol}}$. H_2 has $H_{H_2}=-436\frac{\text{kJ}}{\text{mol}}$. So the net enthalpy change in the reaction is $H_{C_2H_6}-H_{C_2H_4}-H_{H_2}=-124\frac{\text{kJ}}{\text{mol}}$. This is not too far off from the reaction value of $\Delta_r H° = -136.3\frac{\text{kJ}}{\text{mol}}$ but not terribly close either. The approximation that all covalent bonds in any material have the same enthalpy is apparently not terrific.

Also keep in mind that bond enthalpies are tabulated for gases. For liquids and solids, intermolecular interactions cannot be neglected and the bond enthalpies are not enough. For liquids and solids, there are still useful tabulated enthalpies of formation and reaction that can be used and will give better estimates than adding the bond enthalpies.

The bottom line is

- Using enthalpies of reaction is best (when available).
- Using enthalpies of formation and Hess' law is the most convenient compromise, giving nearly identical to reaction enthalpies and requiring less tabulated data.
- Using bond enthalpies is a last resort, only recommended when formation enthalpies are not available.

4.2 Expansion work

A natural question to ask is whether the difference between enthalpy and energy actually even matters. The difference between enthalpy and energy is Δ(PV). To see how big this is, relative to the enthalpy or energy, let's consider some examples.

For a first example, consider chemical reactions in solids. Clam shells have a layer of calcite and a layer of aragonite. These minerals are both naturally occurring forms of calcium carbonate $\mathrm{CaCO_3}$. They both have the same chemical composition, but different crystal structures. Aragonite forms from calcite at high pressure, but at typical pressures on the surface of the earth, aragonite is unstable and turns into calcite on the 10 million year timescale. The two minerals have different densities: aragonite is more dense, at $2.93\frac{g}{\mathrm{cm}^3}$ than calcite at $2.71\frac{g}{\mathrm{cm}^3}$. Thus when aragonite converts into calcite, its volume expands, doing work and an enthalpy $\Delta H = 0.21\frac{\mathrm{kJ}}{\mathrm{mol}}$ is released at $P = 1\,\mathrm{atm}$. The volume change per unit mass is

$$\frac{\Delta V}{m} = \left(\frac{1}{2.71\frac{g}{\mathrm{cm}^3}} - \frac{1}{2.93\frac{g}{\mathrm{cm}^3}}\right) = 0.028\frac{\mathrm{cm}^3}{g} \tag{47}$$

Now 1 mole of $\mathrm{CaCO_3}$ weights 100g, and using $P = 1\,\mathrm{bar} = 10^5\mathrm{Pa} = 10^5\frac{J}{m^3} = 10^{-4}\frac{\mathrm{kJ}}{\mathrm{cm}^3}$ we get

$$P\Delta V = 10^{-4}\frac{\mathrm{kJ}}{\mathrm{cm}^3}\left(0.028\,\frac{\mathrm{cm}^3}{g}\right) \times \frac{100\,g}{\mathrm{mol}} = 2.8 \times 10^{-4}\frac{\mathrm{kJ}}{\mathrm{mol}} \tag{48}$$

So in this case $P\Delta V \ll \Delta H$ and therefore the enthalpy and energy changes are nearly identical. The work done is only a small fraction, 0.1%, of the enthalpy change.

Volume change is more important when the total number of molecules is not the same on both sides of a reaction. For example, consider the enthalpy change in the formation of ammonia gas, $\mathrm{NH_3}$, through the reaction of hydrogen and nitrogen gases:

$$3H_2 + N_2 \rightarrow 2\mathrm{NH_3} \tag{49}$$

This reaction converts 4 molecules into 2, so $\Delta n = -2$, so the volume will go down. Using the ideal gas law at room temperature

$$\Delta(\mathrm{PV}) = (\Delta n)RT = -2\times 8.3\,\frac{J}{\mathrm{mol}\,K} \times 298\,K = -4.9\frac{\mathrm{kJ}}{\mathrm{mol}} \tag{50}$$

Let us compare this to the enthalpy change. Computing the enthalpy change by adding the bond enthalpies gives $\Delta H = -97\,\frac{\mathrm{kJ}}{\mathrm{mol}}$ for this reaction, not far off from the measured reaction enthalpy change of $\Delta_r H^\circ = -91.88\frac{kJ}{\mathrm{mol}}$. So we find that, $\Delta(\mathrm{PV}) = -4.5\frac{\mathrm{kJ}}{\mathrm{mol}}$ is around 5% of the total enthalpy change in this case. 5% is small, but not so small that it can be neglected. Indeed, a 5% change in the energetics can have important effects on reaction kinetics.

In summary, as a rule of thumb, enthalpies and energies are pretty similar for solids and liquids, differing at the less than a percent level, but for gases the difference can be relatively large. The difference between the energy and enthalpy change is essentially given by $\Delta H - \Delta E = (\Delta n)RT$ with Δn the change in the number of moles of *gas*. This is equal to $2.48\frac{\mathrm{kJ}}{\mathrm{mol}}\Delta n$ at room temperature and pressure. These enthalpy changes are included in tabulated enthalpies of formation and reaction (which are different for liquids and gases) and are also included in bond enthalpies (defined for gases and computed by averaging the formation enthalpies of various molecules with that bond).

5 Gibbs free energy

Gibbs free energy is defined as

$$G \equiv H - TS = E + PV - TS \tag{51}$$

The differential of G is

$$dG = dE + d(PV) - d(TS) = VdP - SdT + \mu dN \tag{52}$$

so $G = G(P, N, T)$ and

$$\left(\frac{\partial G}{\partial T}\right)_{P,N} = -S, \qquad \left(\frac{\partial G}{\partial P}\right)_{T,N} = V, \qquad \left(\frac{\partial G}{\partial N}\right)_{P,T} = \mu \tag{53}$$

Gibbs free energy is the constant pressure version of Helmholtz free energy; it is $E - TS$ with E replaced by H. Recall that Helmholtz free energy is useful at constant volume and constant temperature. At constant pressure, as in chemistry and biology, enthalpy and Gibbs free energy are used. Gibbs free energy gives the maximum amount of work that can be done at constant pressure and temperature. At constant pressure and constant temperature, Gibbs free energy has its minimum value at equilibrium.

A powerful function of the Gibbs free energy is that it tells which direction a reaction will go. In a chemical reaction at constant T and P, the amount of heat released is given by the enthalpy change $\Delta_r H$. To get the sign right, note that if $\Delta_r H = H_{\text{prod}} - H_{\text{react}}$ is positive, $\Delta_r H > 0$, then the products have more enthalpy than the reactants, so the surroundings must put in energy and heat is withdrawn. The entropy change in the surroundings (the air or solution or whatever heat bath is fixing T and P in the first place) is $\Delta S_{\text{surround}} = \frac{Q}{T} = -\frac{\Delta_r H}{T}$. The entropy change in the system is $\Delta_r S$ so the total entropy change is $\Delta S = \Delta S_{\text{sys}} + \Delta S_{\text{surround}} = \Delta_r S - \frac{\Delta_r H}{T} = -\frac{\Delta_r G}{T}$. Since total entropy always increases the reaction can only proceed if the Gibbs free energy change is *negative*: $\Delta_r G < 0$. Thus the sign of the Gibbs free energy change indicates which way the reaction will spontaneously proceed.

For an ideal monatomic gas, we want to express G as a function of P, N and T. We start by using Eq. (31) to write

$$G = F + PV = -Nk_B T\left[\ln\frac{V}{N} + \frac{3}{2}\ln\left(\frac{2\pi m T}{h^2}\right) + 1\right] + PV \tag{54}$$

Then we convert V to P using the ideal gas law $V = \frac{Nk_B T}{P}$ so

$$G = -Nk_B T\left[\ln\frac{k_B T}{P} + \frac{3}{2}\ln\left(\frac{2\pi m T}{h^2}\right)\right] \tag{55}$$

Then we find

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{P,T} = k_B T \ln n\lambda^3 \tag{56}$$

with $\lambda = \frac{h}{\sqrt{2\pi m k_B T}}$ the thermal wavelength, in agreement with our previous result. This explicit calculation confirms that for a monatomic ideal gas the chemical potential is the Gibbs free energy per molecule.

Note that we found that $G = \mu N$ for the ideal gas. This relation is actually very general. It follows immediately from the definition $G = E + PV - TS$ and the Euler relation in Eq. (17) (which relied on the extensivity of entropy). When there are multiple species, $G = \sum \mu_i N_i$. Thus, similar to how the partition function and the Helmholtz free energy were equivalent, the chemical potential and the Gibbs free energy are equivalent.

5.1 Partial pressure

If we have a gas with N_1 molecules of type 1 and N_2 molecules of type 2, then they both exert pressure on the walls of the container. We call the pressure due to molecules of type i the **partial pressure** for that type and denote it P_i. The ideal gas law $PV = Nk_B T$ holds for a single gas or for a mixture of gases. So say there are two gases with $N_1 + N_2 = N$. Then by the ideal gas law, the partial pressure of gas one is

$$P_i \equiv \frac{N_i}{V} k_B T \quad \text{(ideal gases)} \tag{57}$$

Since the ideal gas law $PV = Nk_B T$ holds for the whole mixture, we can divide by it giving

$$\boxed{\frac{P_i}{P} = \frac{N_i}{N}} \tag{58}$$

This relation is called **Dalton's law**. We derived it for ideal gases where the pressure is linear in the number density but it also holds empirically for many interacting systems such as liquids.

Next we can define the **partial Gibbs free energy** for one monatomic ideal gas in a mixture as that for a single gas, with N replaced by N_i and P replaced by P_i:

$$G_i = -N_i k_B T\left[\ln\left(\frac{k_B T}{P_i}\right) + \frac{3}{2}\ln\left(\frac{2\pi m T}{h^2}\right)\right] \tag{59}$$

This definition is useful because it makes Gibbs free energy extensive:

$$G = G_1 + G_2 + \cdots \tag{60}$$

To check this, consider mixing two gases with the same mass, like He^3 and He^4 gas, with $N_1 = N_2 = \frac{N}{2}$. Then $\frac{N}{N_i} = 2$

$$G_1 + G_2 = -N k_B T\left[\ln\left(2\frac{k_B T}{P}\right) + \frac{3}{2}\ln\left(\frac{2\pi m T}{\hbar^2}\right)\right] \tag{61}$$

$$= -N k_B T\left[\ln\frac{k_B T}{P} + \frac{3}{2}\ln\left(\frac{2\pi m T}{\hbar^2}\right)\right] - N k_B T \ln 2 \tag{62}$$

The first term on the second line is the Gibbs free energy for a gas of N identical particles of mass m. The final term can be written as$-N k_B T \ln 2 = -T\Delta S$, where $\Delta S = N k_B \ln 2$. This extra term is exactly the entropy of mixing. It is part of the Gibbs free energy since the mixed system comprises two different types of particles, and so has more entropy (and less Gibbs free energy), then a single homogeneous gas.

5.2 Law of mass action

Now we want to generalize away from a monatomic ideal gas to an arbitrary mixture of general ideal gases. We can write the partition function for a single molecule of an ideal gas as

$$\zeta = Z_{\text{single molecule}} = \sum_{\varepsilon} e^{-\beta\varepsilon} = \int \frac{d^3x\, d^3p}{h^3} \sum_{\text{internal states j}} e^{-\beta\left(\frac{\vec{p}^2}{2m} + \varepsilon_j\right)} \tag{63}$$

The energy ε_j includes all contributions to the energy other than momentum. For example, including chemical binding energy ε_b, kinetic degrees of freedom and a vibrational mode of frequency ω

$$\zeta = V e^{-\beta\varepsilon_b}\left(\frac{2\pi m}{\beta h^2}\right)^{\frac{3}{2}} \frac{1}{2\sinh\left(\frac{\beta}{2}\hbar\omega\right)} = \frac{V}{\lambda^3} e^{-\beta\varepsilon_b} \frac{1}{2\sinh\left(\frac{\beta}{2}\hbar\omega\right)} \tag{64}$$

The volume factor comes from the d^3x integral. This integral is always there, so ζ will always scale linearly with V. A key element of ζ is the binding energy ε_b which must be treated with a consistent zero-point for all the molecules involved in the mixture. In general ζ is complicated for molecules, and we will not try to compute it. As we'll see, we don't need to, because we can measure it. The binding energy part is included in the standard enthalpy of formation that we can look up.

If there are N_1 molecules, then the possible total energies are sums of the energies of the individual molecules. The partition function is then the product of the single particle partition functions divided by the identical particle factor $N_1!$:

$$Z_1 = \frac{1}{N_1!} \sum_{\varepsilon_1 \cdots \varepsilon_{N_1}} e^{-\beta(\varepsilon_1 + \varepsilon_2 + \cdots + \varepsilon_{N_1})} = \frac{1}{N_1!}(Z_{\text{singlemolecule}})^{N_1} = \frac{1}{N_1!}\zeta_1^{N_1} \tag{65}$$

If there are two gases, we multiply their partition functions. So

$$Z = Z_1 Z_2 = \frac{1}{N_1!}\zeta_1^{N_1} \frac{1}{N_2!}\zeta_2^{N_2} \tag{66}$$

That the partition function is multiplicative in this way follows from assuming the gases are non-interacting: the energy of each molecule is independent of the other molecules. We are not making any other assumption about the molecules though, such as how many degrees of freedom there are.

The Helmholtz free energy of the two gas mixture is then

$$F = -k_B T \ln Z \approx -k_B T\left[N_1\left(\ln\frac{\zeta_1}{N_1} + 1\right) + N_2\left(\ln\frac{\zeta_2}{N_2} + 1\right)\right] \tag{67}$$

where Stirling's relation $N! \approx e^{-N}N^N$ was used in the $\approx$ step. The chemical potential for gas 1 is then

$$\mu_1 = \left(\frac{\partial F}{\partial N_1}\right)_{T,V,N_2} = -k_B T \ln\frac{\zeta_1}{N_1} \tag{68}$$

and similarly for gas 2. To make sure we haven't messed anything up, the Gibbs free energy is

$$G = F + PV = -k_B T\left[N_1\left(\ln\frac{\zeta_1}{N_1} + 1\right) + N_2\left(\ln\frac{\zeta_2}{N_2} + 1\right)\right] + \underbrace{(N_1 + N_2)k_B T}_{\text{from ideal gas law}} \tag{69}$$

$$= \mu_1 N_1 + \mu_2 N_2 \tag{70}$$

so that $G = \sum_i \mu_i N_i$ as expected.

It is helpful to express the chemical potential in terms of the total number of particles and the fraction $\frac{N_i}{N}$. We can easily do this by rewriting the logarithm in Eq. (68):

$$\mu_i = -k_B T \ln\frac{\zeta_i}{N_i} = -k_B T \ln\frac{\zeta_i}{N} + k_B T \ln\frac{N_i}{N} \tag{71}$$

$$= -k_B T \ln\frac{k_B T \zeta_i}{PV} + k_B T \ln\frac{N_i}{N} \tag{72}$$

Thus,

$$\boxed{\frac{N_i}{N} = \exp\left[\frac{\mu_i - G_{0i}}{k_B T}\right]} \tag{73}$$

where, using $N = \frac{PV}{k_B T}$,

$$G_{0i} = -k_B T \ln\left[\frac{k_B T}{P}\left(\frac{\zeta_i}{V}\right)\right] \tag{74}$$

G_{0i} is the Gibbs free energy for a molecule in a mixture. For a single molecule $N_i = N = 1$ and so $G_{0i} = \mu_i = 1 \times G$. Although G_{0i} appears to depend on V, actually it does not, since since ζ_i is directly proportional to V as in Eq. (64). Note that, critically, G_{0i} depends on the total pressure P not the partial pressure P_i. If G_{0i} were written in terms of the partial pressure then it would be the partial Gibbs free energy per particle:

$$\frac{G_i}{N_i} = -k_B T \ln\left[\frac{k_B T}{P_i}\left(\frac{\zeta_i}{V}\right)\right] = \mu_i \tag{75}$$

The difference between $N_i G_{0i}$ and G_i is exactly the entropy of mixing terms, as in Eq. (62).

Eq. (73) is like the relation $n = \frac{1}{\lambda^3}\exp\left(\frac{\mu - \varepsilon}{k_B T}\right)$ we derived last lecture for a monatomic ideal gas. Indeed,if you substitute $\zeta_i = \frac{V}{\lambda^3}e^{-\beta\varepsilon_b}$ for a monatomic ideal gas, you can check that Eq. (73) reduces to $n_i = \frac{1}{\lambda^3}\exp\left(\frac{\mu_i - \varepsilon_b}{k_B T}\right)$ exactly. The difference is Eq. (73) is more general than monatomic ideal gases. We have also written the formula in terms of the fraction $\frac{N_i}{N}$ rather than $n_i = \frac{N_i}{V}$ and we have G_{0i} written with pressure explicit rather than volume (so we can hold P fixed).

From here we get a relation between the fractions of reactants. Let us use the notation

$$x_j \equiv \frac{N_j}{N} \tag{76}$$

for the molar fraction of a reactant. Then, for something like

$$2A + 3B \rightleftharpoons 7C \tag{77}$$

for which $2\mu_A + 3\mu_B = 7\mu_C$ we would find that the μ_i drop out from the combination

$$\frac{x_C^7}{x_A^2 x_B^3} = \exp\left[-\frac{\Delta_r G_0}{k_B T}\right] \tag{78}$$

this is the **law of mass action**. In the general form, the powers on the left hand side are determined by the stoichiometric coefficients in the reaction equation and $\Delta_r G_0$ is the change in Gibbs free energy per particle (i.e. $\Delta_r G_0 = 7G_{0A} - 2G_{0B} - 3G_{0C}$ for this example).

Recall that we derived the law of mass action in the previous lecture for monatomic ideal gases, where the exponent had the energy change $\Delta\varepsilon$ per particle and the left hand side had the concentrations $[A] = \frac{N_j}{V}$ rather than the molar fractions. That previous formula is a special case of this more general mass action formula, as you can check.

To understand the law of mass action, recall that the *total* Gibbs free energy change in a reaction at equilibrium is zero, $\Delta G = 0$; otherwise, G could be minimized by moving molecules from one side to another. The overall ΔG has a part *per molecule*, which is the Gibbs reaction energy $\Delta_r G$ and a part that depends on the concentrations, encoded in the x_i fractions. This second part is entirely entropic, driven by the entropy of mixing, Thus the law of mass action says that in equilibrium these two contributions to ΔG exactly cancel. It thereby lets us figure out the equilibrium concentrations from the Gibbs reaction energy per particle.

By Dalton's law, we also have $x_i = \frac{P_i}{P}$ so Eq. (78) can also be thought of as an equation for the equilibrium partial pressures. Chemists also prefer to use moles rather than particles, so we use $\Delta_r G$, the **Gibbs reaction energy** (in $\frac{\text{kJ}}{\text{mol}}$) and use RT instead of $k_B T$. The ratio of fractions is also given a name, **the equilibrium constant** and the symbol K:

$$K \equiv \frac{x_C^7}{x_A^2 x_B^3} = \frac{\left(\frac{N_C}{N}\right)^7}{\left(\frac{N_A}{N}\right)^2 \left(\frac{N_B}{N}\right)^3} = \frac{1}{P^4}\frac{P_C^7}{P_A^2 P_B^3} = e^{-\frac{\Delta_r G_0}{k_B T}} = e^{-\frac{\Delta_r G}{RT}} \tag{79}$$

Let's do an example. In the reaction $H_2O(g) \rightleftharpoons H_2(g) + \frac{1}{2}O_2(g)$ at $T = 5000K$ the Gibbs reaction energy is $\Delta_r G = 118\frac{\text{kJ}}{\text{mol}}$. If we start with 1 mol of H_2O it will decompose into α moles of H_2 and $\frac{\alpha}{2}$ moles of O_2 leaving $1 - \alpha$ moles of H_2O. The total number of moles is $1 - \alpha + \alpha + \frac{\alpha}{2} = 1 + \frac{\alpha}{2}$. Then

$$\frac{x_{H_2} x_{O_2}^{1/2}}{x_{H_2O}} = \frac{\left(\frac{\alpha}{1+\frac{\alpha}{2}}\right)\sqrt{\frac{\alpha}{2\left(1+\frac{\alpha}{2}\right)}}}{\frac{1-\alpha}{1+\frac{\alpha}{2}}} = \exp\left[-\frac{118\frac{\text{kJ}}{\text{mol}}}{8.3\frac{J}{\text{mol}\,K} \times 5000K}\right] = 0.058 \tag{80}$$

Solve numerically for α gives $\alpha = 0.17$. Thus at 5000K, 17% of the water molecules will be decomposed into H_2 and O_2. At room temperature $\Delta_r G = 228\frac{\text{kJ}}{\text{mol}}$ and $\alpha = 10^{-27}$.

This example indicates an important qualitative point about using the Gibbs free energy: generally $\Delta_r G$ is of order hundreds of $\frac{\text{kJ}}{\text{mol}}$ while $RT = 2.5\frac{\text{kJ}}{\text{mol}}$ at room temperature. So the factor $\exp\left(-\frac{\Delta_r G}{RT}\right)$ is almost always either very very small, if $\Delta_r G > 0$ or very very large if $\Delta_r G < 0$. Thus for **exergonic** reactions ($\Delta_r G < 0$), the reaction strongly favors the products, while for **endergonic** reactions ($\Delta_r G > 0$), the reactants are favored. Thus to a good approximation, we can use the rule of thumb that

- If we mix some chemicals, the sign of $\Delta_r G$ tells which way the reaction will go.

This rule of thumb works only when the concentrations are not exponentially small so that the $\exp\left(-\frac{\Delta_r G}{RT}\right)$ dominates. Of course, if the system is in equilibrium, it will not proceed in any direction. Or if the concentration of products (or reactants) is small enough, the reaction will proceed in the only direction it can. In such a case, when the reaction proceeds against the direction of $\Delta_r G$, the total Gibbs free energy of the system is still decreasing: the entropy of mixing associated with the concentration imbalance dominates over the $\Delta_r G$ effect from the reaction itself (remember, we pulled the concentration-dependence out in Eq.(71)).

In summary, the law of mass action always tells us which way the reaction will proceed given some initial concentrations. The rule-of-thumb only determines the reaction direction when the concentrations are not exponentially small.

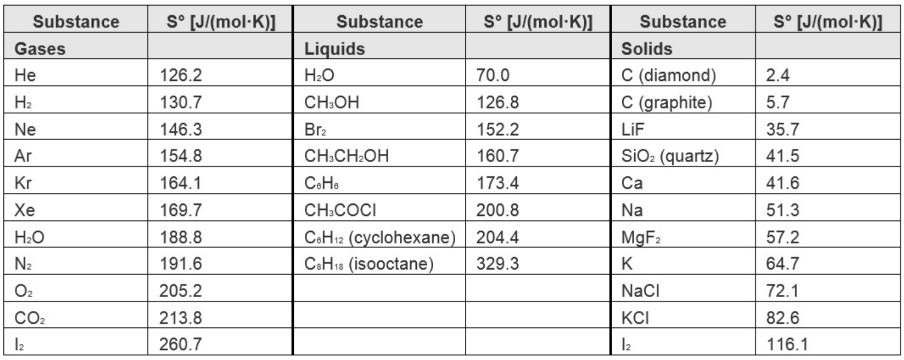
5.3 Direction of chemical reactions

We saw that the direction a reaction proceeds is determined by the sign of $\Delta_r G$. What do we know about this sign? Although G_{0i} and $\Delta_r G$ are in principle computable from the partition function for a single molecule, this is never actually done. One can easily look up $\Delta_r G$ under standard conditions $P = 1\,\text{bar}$ and $T = 298K$. This standard value of the Gibbs reaction energy is denoted $\Delta_r G°$. It is more useful however to look up $\Delta_r H$ and $\Delta_r S$ and compute $\Delta_r G$ via:

$$\Delta_r G = \Delta_r H - T\Delta_r S \tag{81}$$

The reason this formula is useful is because both $\Delta_r H$ and $\Delta_r S$ are generally *weakly* dependent on temperature (less then any power of T), while $\Delta_r G$ *depends strongly on* T because of the explicit factor of T in Eq. (81). So Eq. (81) lets us compute $\Delta_r G$ at any temperature, while $\Delta_r G°$ only gives the value at one reference temperature.

The dominant contribution to $\Delta_r H$ is from bonds breaking and forming, with a subleading contribution from $\Delta(\text{PV}) \approx \Delta n_{\text{gas}} RT$. What determines $\Delta_r S$? Or more practically, how can we measure $\Delta_r S$? One way is to ask at what temperature the reaction is in equilibrium. Then we know $\Delta_r G = 0$ and we can compute $\Delta_r S = \frac{\Delta_r H}{T}$. Alternatively, we could note the heat Q given off in the reaction and use $\Delta S_{\text{surroundings}} = \frac{Q}{T}$; if we can reverse the reaction adiabatically and isothermally doing work W, then $\Delta S = \frac{Q - W}{T}$. Conveniently, chemists have measured the entropy of enough reactions to tabulate **standard molar entropies.** For example,



Substance	S° [J/(mol·K)]	Substance	S° [J/(mol·K)]	Substance	S° [J/(mol·K)]
Gases		**Liquids**		**Solids**	
He	126.2	H_2O	70.0	C (diamond)	2.4
H_2	130.7	CH_3OH	126.8	C (graphite)	5.7
Ne	146.3	Br_2	152.2	LiF	35.7
Ar	154.8	CH_3CH_2OH	160.7	SiO_2 (quartz)	41.5
Kr	164.1	C_6H_6	173.4	Ca	41.6
Xe	169.7	CH_3COCl	200.8	Na	51.3
H_2O	188.8	C_6H_{12} (cyclohexane)	204.4	MgF_2	57.2
N_2	191.6	C_8H_{18} (isooctane)	329.3	K	64.7
O_2	205.2			NaCl	72.1
CO_2	213.8			KCl	82.6
I_2	260.7			I_2	116.1

Figure 3. Standard molar entropies for some compounds at 298 K

Then the change in entropies can be computed by taking the difference of the standard molar entropies of the products and reactants. Note from the table that

- More complex molecules have higher entropies.
- Gases have higher entropies than liquids which have higher entropies than solids.

These observations are consistent with our understanding of entropy as measuring disorder.

Let's consider an example. **Limestone** is a commonly occurring mineral, calcium carbonate $CaCO_3$. By itself, limestone is not so useful, but can be converted to **lime**, calcium oxide CaO in a kiln. Lime is an extremely useful mineral, used in making steel, mortar and cement and in agriculture. To make lime from limestone involves the reaction

$$\text{CaCO}_3 \leftrightharpoons \text{CaO} + \text{CO}_2 \tag{82}$$

The enthalpy change in this reaction is $\Delta_r H = 178\,\frac{\text{kJ}}{\text{mol}}$.The entropy change is $\Delta_r S = 161\frac{J}{K\,\text{mol}}$. At room temperature, $T = 298K$, so

$$\Delta_r G = \Delta_r H - (298K)\,\Delta_r S = 130\,\frac{\text{kJ}}{\text{mol}} \tag{83}$$

Since the reaction increases the Gibbs free energy, it does not spontaneously occur.

On the other hand, if we heat the limestone in a lime kiln, to $T = 1500K$, then

$$\Delta_r G = \Delta_r H - (1500K)\,\Delta_r S = -64\,\frac{\text{kJ}}{\text{mol}} \tag{84}$$

Thus the kiln allows the reaction to occur. Note that there is also some temperature dependence to $\Delta_r H$ from $\Delta(\text{PV}) = \Delta n k_B T = RT = 8.3\frac{J}{K\,\text{mol}}$. Since $\Delta(\text{PV}) \ll \Delta_r S$ we can neglect the temperature dependence of $\Delta_r H$ compared to $T\Delta_r S$ term.

Normally heating up a system makes a reaction go faster. Taking milk out of the fridge makes it go bad faster. But milk would go bad eventually even if left in the fridge. With the lime kiln, heating the system does not just make the reaction go faster. *It changes the direction of the reaction.* The reverse reaction naturally occurs at room temperature – lime will eventually turn back into limestone if left in the presence of CO_2.

Note that we have assumed that all of the T dependence is in the explicit factor of T in the definition $\Delta_r G = \Delta_r H - T\Delta_r S$. What about the temperature dependence of $\Delta_r H$ and $\Delta_r S$ themselves? We can write $\Delta_r H = \Delta_r E + \Delta_r(\text{PV})$. The $\Delta_r E$ contribution is from breaking bonds, which is independent of T. Solids and liquids have the same volume, so $\Delta_r(\text{PV}) = (\Delta n_{\text{gas}})RT \approx 8\frac{J}{\text{mol}\,K}\Delta n_{\text{gas}}T$. Although this depends linearly on T, just like the $T\Delta_r S$ factor in $\Delta_r G$, the numerical values for $\Delta_r S \approx 161\frac{J}{\text{mol}\,K}$ in this example are much bigger. Thus we can neglect the temperature dependence of $\Delta_r H$ when solids and liquids are involved; for gases, it is a subleading effect. The temperature dependence of $\Delta_r S$ is generally logarithmic, since $S \sim N k_B \ln T$ and generally very small.

In the above discussion of $CaCO_3$ we used only the sign of $\Delta_r G$ to determine the reaction direction. The law of mass action tells us the relative concentrations in equilibrium

$$K = \frac{x_{\text{CaO}}\, x_{\text{CO}_2}}{x_{\text{CaCO}_3}} = \exp\left[-\frac{\Delta_r G}{k_B T}\right] \tag{85}$$

For $T = 298K$, $K = \exp\left(-\frac{130}{0.0083 \times 293}\right) = 10^{-25}$ and $T = 1500K$, $K = \exp\left(\frac{65}{8.3 \times 1.5}\right) = 185$, so we see that the equilibrium concentrations are hugely different at these two temperatures.

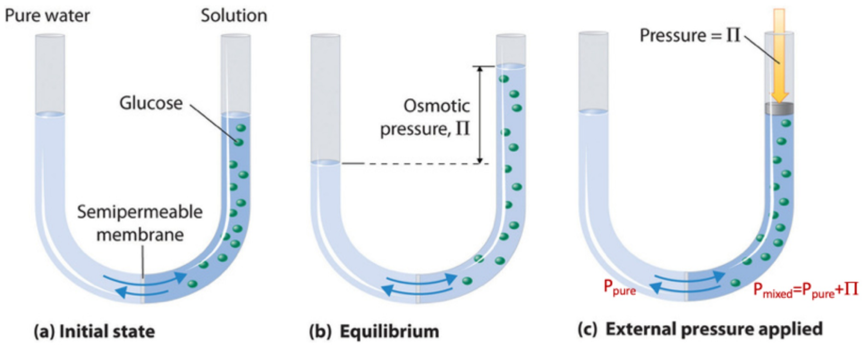
Suppose the system is in equilibrium at some temperature. Then if we add more CaO to the system, x_{CaO} will go up. To keep K the same, the system will adjust to remove CaO and increase $CaCO_3$. This is an example of a phenomenological observation called

- **Le Chatelier's principle**: a system will work to restore equilibrium by counteracting any change.

6 Osmotic pressure

As a final example, let us return to the topic of osmotic pressure, introduced in the discussion of entropy of mixing. Osmotic pressure is the pressure resulting from a concentration imbalance on the two sides of a semi-permeable barrier. For example, if you put a raisin in water, the higher sugar content of the raisin as compared to the water forces the water to be drawn into the raisin. The result is that the raisin swells up, almost back to the size of a grape. The drying out of a grape is also osmosis: water flows out of the grape into the air over time, and the grape desiccates. Grocers spray water on their fruits and vegetables to increase the local concentration of water so their produce looks more appealing. How about your fingers getting wrinkled when you stay in the bath too long. Is this osmosis?

Say we have water in a U-shaped tube with a semi-permeable membrane in the middle. The membrane allows water to pass but not sugar. Now put some sugar on one side. As water flows into the sugar side, it will increase the pressure on that side, lowering the pressure on the other side. Thus the sugar water will move up. This is a physical effect due to the entropy of mixing.



(a) Initial state **(b) Equilibrium** **(c) External pressure applied**

Figure 4. Osmotic pressure arises when concentrations are different on two sides of a semi-permeable barrier. Adding glucose to one side causes a pressure imbalance. This can be compensated by applying an external pressure Π called the osmotic pressure.

One way to quantify the effect is by the pressure you need to apply on the sugary side to restore the balance. This pressure is called the **osmotic pressure** and denoted by the symbol Π.

To compute the osmotic pressure, let us start with some definitions. A **solution** is a mixture of **solvent** and **solute**, with the solvent being the major component and the solute being a small addition. For example, in sugar water, water is the solvent and sugar the solute.

We want to compute the chemical potential of the solvent (water) on both sides, which we can derive from the Gibbs free energy accounting for the entropy of mixing. Let us say that initially there is the same number N_w of solvent (water) molecules on both sides of the barrier and we then add N_s solute (sugar) molecules to one side.

Recall that entropy of mixing is the extra entropy that a mixed substance has compared to a pure substance with the same properties (N, T, P). A great thing about the entropy of mixing is that it only depends on whether the things mixing are indistinguishable, not any other other properties of those things (internal degrees of freedom, etc.). For N particles in a volume V, the entropy is $S = k_B \ln\left(\frac{1}{N!}V^N\right) \approx -k_B N \ln\frac{N}{V}$. For our N_w molecules of solvent (water) and N_s molecules of solvent, the entropy of mixing is

$$\Delta S_{\text{mix}} = -k_B\left[\underbrace{\left(N_w \ln\frac{N_w}{V} + N_s \ln\frac{N_s}{V}\right)}_{\text{mixed system}} - \underbrace{(N_w + N_s)\ln\left(\frac{N_w + N_s}{V}\right)}_{\text{pure system with } N_w + N_s \text{particles}}\right] \tag{86}$$

$$= -k_B\left[N_w \ln\frac{N_w}{N_w + N_s} + N_s \ln\frac{N_s}{N_w + N_s}\right] > 0 \tag{87}$$

Note that V dropped out. Indeed, the entropy of mixing only depends on the $\frac{1}{N!}$ factor.

In the limit that $N_s \ll N_w$ we can expand in $\frac{N_s}{N_w}$ to find

$$\Delta S_{\text{mix}} = k_B N_s\left(1 - \ln\frac{N_s}{N_w}\right) + \mathcal{O}\left(\frac{N_s^2}{N_w}\right) \tag{88}$$

Let's write $G_w(T,P)$ for the Gibbs free energy of pure solvent (water). Since $N_s \ll N_w$, the enthalpy of the solute gives a negligible contribution to the total Gibbs free energy, and the only contribution that matters is from the entropy of mixing. So the total Gibbs free energy on the mixed side, generalizing Eq. (62), is

$$G_{\text{mixed}} = G_w - T S_{\text{mix}} = G_w - k_B T N_s\left(1 - \ln\frac{N_s}{N_w}\right) \tag{89}$$

Thus the chemical potential of the solvent on the mixed side is then

$$\mu_w^{\text{mixed}}(T,P) = \left(\frac{\partial G_{\text{mixed}}}{\partial N_w}\right)_{T,P,N_s} = \mu_w(T,P) - k_B T\frac{N_s}{N_w} \tag{90}$$

where $\mu_w(T,P)=\frac{G_w}{N_w}$ is the chemical potential of the pure solvent.

Equilibrium requires the chemical potential of the solvent to be the same on both sides of the barrier. So

$$\mu_w(T,P_{\text{pure}})=\mu_w^{\text{mixed}}(T,P_{\text{mixed}})=\mu_w(T,P_{\text{mixed}})-k_BT\frac{N_s}{N_w} \tag{91}$$

The osmotic pressure we are trying to compute is the pressure difference $\Pi=P_{\text{mixed}}-P_{\text{pure}}$. In the limit $N_s\ll N_w$ we must have $\Pi\ll P_{\text{pure}}$ so that we can expand

$$\mu_w(T,P_{\text{mixed}})=\mu_w(T,P_{\text{pure}}+\Pi)=\mu_w(T,P_{\text{pure}})+\Pi\left(\frac{\partial\mu_w}{\partial P}\right)_{T,N_w} \tag{92}$$

Since $G_w=\mu_wN_w$,

$$\left(\frac{\partial\mu_w}{\partial P}\right)_{T,N_w}=\frac{1}{N_w}\left(\frac{\partial G_w}{\partial P}\right)_{T,N_w}=\frac{V}{N_w} \tag{93}$$

Combining the last 3 equations gives

$$\mu_w(T,P_{\text{pure}})=\mu_w(T,P_{\text{pure}})+\Pi\frac{V}{N_w}-k_BT\frac{N_s}{N_w} \tag{94}$$

So that

$$\boxed{\Pi=k_BT\frac{N_s}{V}} \tag{95}$$

This is known as **van 't Hoff's formula**.

You might notice that this formula for the pressure increase is the same as the ideal gas law $P=k_BT\frac{N}{V}$. Indeed, if you used gases rather than liquids and solids, and added some gas to the right hand side at constant volume, of course the pressure would go up. The increase in pressure, at fixed T and V would be exactly the partial pressure of the new gas added, $P^{\text{new}}=k_BT\frac{N_{\text{new}}}{V}$. Van 't Hoff's formula is easy to understand for gases. The amazing thing however is that it applies for liquids and solids too. To see why, recall that an ideal gas is one where we can neglect intermolecular interactions. This leads to features like the energy is extensive, scaling linearly with the number density $E\sim n$. If pairwise intermolecular interactions dominated then we would expect $E\sim n^2$. In water or other liquids, interactions are important, so there are non-extensive contributions to the energy, like surface tension. Now, interactions between a solute (sugar) and solvent (water) can certainly be strong. The key point however is that as long as the solute is dilute, the solute/solvent interactions will be rare: any N_s^2 scaling in thermodynamic properties will be subdominant to the ideal gas N_s scaling: if we write $E\sim c_0+c_1N_s+c_2N_s^2$, we can always make N_s small enough so that $E\sim c_0+c_1N_s$ is a good approximation. So for dilute solutes, the N_s dependence is always linear, and approaches ideal, extensive, scaling behavior. This is the ultimate origin of the universality of the van 't Hoff formula even for mixtures of liquids, and solids, and non-ideal gases. The key assumption is that $N_s\ll N_w$: the solute is dilute.

You can repeat this exercise when the solute contains a number of different substances (sugar, salt, etc). The result is that the osmotic pressure is

$$\Pi=k_BT\sum_s\frac{N_s}{V} \tag{96}$$

This indicates that osmotic pressure is a **colligative property**, meaning it doesn't matter what the solute is, just the total concentration of solutes.

For example, when your blood pressure is 120/80 it means that the pressure measured is 120 mmHg=0.16 atm coming out of your heart and 80 mmHg=0.1 atm going in. This doesn't mean that your blood is at much lower than atmospheric pressure, since it is measured by a device in the atmosphere – these numbers are *relative* to atmospheric pressure; thus the actual pressure in your veins is 1.1 to 1.16 atm. The osmotic pressure in blood is 7.65 atm at $37°C=310K$. This doesn't mean that blood is under 7.65 atm of pressure; it means that if a blood vessel were immersed in pure water, 7.65 atm would have to be applied to prevent the influx of water. Blood vessels are not surrounded by water, but by solution, also at an osmotic pressure around 7.65, so no solution flows.

We can use these numbers to find the net concentration n_s (in mol/L) of all dissolved solvents:

$$n_s = \frac{N_s}{N_A \cdot V} = \frac{\Pi}{RT} = \frac{7.65\,\text{atm}}{0.08314 \frac{L\,\text{atm}}{\text{mol}\,K} 310\,K} = 296\,\frac{\text{mmol}}{L} \tag{97}$$

where mmol is a millimole, and we have divided by Avogadro's number N_A to get an expression in terms of mols. This quantity n_s is called the **osmolarity** and often written in millimoles per kg of solution (water): $n_s = 296\,\frac{\text{mmol}}{L} = 296\frac{\text{mmol}}{\text{kg}}$. For example, we can compare to the osmolarity of $50g$ of sugar (glucose, molar mass 180 $\frac{\text{g}}{\text{mol}}$) mixed into 1 liter of water:

$$n_s = \frac{50g}{180\,\frac{g}{\text{mol}}} \frac{1}{L} = 277\frac{\text{mmol}}{L} \tag{98}$$

So mixing a little more than $50g$ of sugar (about 2 tablespoons) with a liter of water and drinking it will not increase your blood pressure. More sugar (or salt) than this concentration will cause your blood pressure to go up.

Osmotic pressure really is an *entropic effect*. It is a powerful example of the importance of entropy. You might have been concerned from time to time that the way we were defining entropy had some arbitrariness to it, due to the choice to coarse-grain or add indistinguishable particle factors. Osmotic pressure indicates that entropy is real and unambiguous. It has physical observable consequences and makes quantitative predictions that can be tested experimentally. Add salt and the pressure goes up and work can be done.

Finally, it is worth pointing out that equilibrium properties, such as from equating the chemical potentials on two sides of a semipermeable barrier, do not tell us anything about the microscopic mechanism by which equilibrium is achieved. Diffusion (Lecture 2) involving the random walks of molecules, is one way. Another is convection, when large macroscopic currents, such as temperature gradients, push the molecules around together. There is also advection, whereby the motion of one type of molecule pulls another along with it. Capillary action is another transport mechanism relevant for liquids where surface tension draws water into a straw or a paper towel. Imbibation is a transport phenomenon in solids or colloids whereby the a material expands as liquid is absorbed (such as a sponge or seed). What is the microscopic mechanism for osmosis? Probably some combination of the above. The point, however, is that the microscopic mechanism is irrelevant. Equilibrium thermodynamics lets us compute the main result, the osmotic pressure, independently of the microscopic mechanism of osmosis.

Test your understanding: In going from step (a) to step (b) in Fig. 4, an amount of water is mixed with the saltwater and entropy increases. When we apply a pressure Π to restore the original levels in the U-tube as in step (c), we are unmixing the amount of water, undoing the entropy of mixing. What compensates for this decrease in entropy so that the second law still holds? Is anything different about the water in the left tube in panels (a) and (c) of Fig. 4?

7 Grand free energy

There is one more free energy that is used sometimes, called the grand free energy Φ. We're not going to use it until Lecture 11, because it's harder to interpret physically, but I include the relevant formulas here since they are closely related to the other free energies from this lecture.

Recall that the grand canonical partition function is

$$\mathcal{Z}(V, T, \mu) = \sum_k e^{-\beta\varepsilon_k + \beta\mu N_k} \tag{99}$$

where the sum is over microstates k with N_k particles and energy ε_k. We also showed that

$$-k_B T \ln\mathcal{Z} = \langle E \rangle - TS - \mu \langle N \rangle \tag{100}$$

We then define the **grand free energy** Φ like the free energy F, but computed using the grand canonical ensemble.

$$\Phi = -k_B T \ln\mathcal{Z} \tag{101}$$

Thus,

$$\Phi(T,V,\mu)=\langle E\rangle - TS-\mu\langle N\rangle \tag{102}$$

Recall that $F(V,T,N)$ and now we have $\Phi(V,T,\mu)$, so the grand free energy has traded N for μ in the free energy. This is similar to how we used $F(V,T,N)=E-TS$ to trades entropy for temperature using $E(S,V,N)$. Indeed, we can also write

$$\Phi(T,V,\mu)=F-\mu N \tag{103}$$

Using Eq. (1) again, we find

$$\boxed{d\Phi=-SdT-PdV-Nd\mu} \tag{104}$$

An important property of Φ is that it is an extensive (like the other energies, internal energy, Helmholtz free energy, Gibbs free energy) function of only a single extensive variable V. Thus it must be proportional to V. Since $\frac{\partial\Phi}{\partial V}\Big|_{\mu,T}=-P$ we then have

$$\Phi=-PV \tag{105}$$

This is a useful relation, similar to $G=\mu N$ for the Gibbs free energy. Like $G=\mu N$, $\Phi=-PV$ follows from the Euler relation in Eq. (17). We'll use the grand free energy in quantum statistical mechanics. It is not used in chemistry or for pure thermodynamics computations, since we can just use PV. I only include it here since it is a free energy and naturally part of the "free energy" lecture. We'll only need the definition Eq. (101) and the relation (104) in future applications.

8 Summary

Free energy is a very important, very general concept in physics. The basic kind of free energy is

- Helmholtz free energy: $F=E-TS$

It represents what we intuitively think of as energy in a thermal system. For example, we intuitively think of energy being minimized, as a ball rolls to the bottom of a hill and stops. But energy, E, is conserved. What is really being minimized is F. The minimization happens actually because entropy S is being maximized. Thus, F is a very general, very useful quantity that can be minimized to find the equilibrium state of the system.

Many physical, biological and chemical systems are at constant pressure. In such circumstances, there is an extra contribution to the free energy and it is more convenient to use

- Enthalpy $H=E+PV$ instead of E
- Gibbs free energy $G=H-TS$ instead of F

The extra PV factor in the definition of enthalpy seamlessly includes the effect of work done when the volume changes at constant pressure. In chemistry and biology, enthalpy and Gibbs free energy rule. When a reaction occurs, we care more about the enthalpy change than the energy change. The biggest difference between enthalpy and energy is for reactions which change in the number of moles of molecules in the gaseous phase, Δn. Then $\Delta H-\Delta E=\Delta\mathrm{PV}=(\Delta n)RT$. This difference comes from the extra work that has to be done when the gas expands against the constant pressure. Enthalpy changes have been measured for many reactions. If they are not known, they can be approximated using differences in molecular enthalpies or approximate bond enthalpies.

We used free energy to derive a number of important results from chemistry. If a reaction can lower the Gibbs free energy, it will occur. If it only increases G, it will not occur. The equilibrium state minimizes G. One important consequence is the law of mass action which determines the equilibrium concentrations of chemicals based on their relative Gibbs free energies. Another is Le Chatelier's principle: a system will work to restore equilibrium by counteracting any change.

Finally, we discussed osmotic pressure. Osmotic pressure is an entropic effect. If you put a grape in a glass of water, water will be drawn into the grape, increasing its pressure. The pressure increase Π is given by van 't Hoff's formula $\Pi=k_BT\frac{N_s}{V}$. This is, not coincidentally, the form for the partial pressure of an ideal gas. The solute acts like an ideal gas because it's dilute in the solvent: any contributions scaling like N_s^2 are subdominant and can be neglected.