Supplemental Material, Chem. 481, Fall 2019

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CONTENTS

I. BASIC DERIVATIVES, INTEGRALS, AND SERIES EXPANSIONS

You should know (and know how to use) the following set of basic derivatives, power series expansions, and integrals

A. Derivatives

$$\frac{dx^n}{dx} = nx^{n-1} \qquad \frac{d\ln[f(x)]}{dx} = \frac{1}{f(x)}\frac{df(x)}{dx}$$

$$\frac{d\exp[f(x)]}{dx} = \exp[f(x)]\frac{df(x)}{dx} \qquad \frac{d\sin(kx)[\cos(kx)]}{dx} = k\cos(kx)[-k\sin(kx)]$$

B. Integrals

$$\int x^n\,dx = \frac{1}{n+1}x^{n+1}$$

$$\int \frac{1}{x}dx = \ln x$$

$$\int \exp(ax)\,dx = \frac{1}{a}\exp(ax)$$

$$\int x\exp(ax^2)\,dx = \frac{1}{2a}\exp(ax^2)$$

$$\int u(x)dv(x) = u(x)v(x) - \int v(x)du(x)$$

The last equation on the right hand side is the general integration by parts expression. As an example suppose $u(x) = x$ and $v(x) = \sin x$. Then, $du(x) = dx$ and $dv(x) = \cos x$, so that

$$\int x\cos x\,dx = x\sin x - \int \sin x dx = x\sin x + \cos x$$

C. Binomial Series

$$(x+y)^2 = x^2 + 2xy + y^2$$
$$(x+y)^3 = x^3 + 3x^2y + 3xy^2 + y^3$$

$$(x+y)^n = x^n + nx^{n-1}y + \frac{n(n-1)}{1\cdot 2}x^{n-2}y^2 + \ldots + \frac{n(n-1)\ldots(n-m+1)}{1\cdot\ 2\ldots(m-1)\cdot m}x^{n-m}y^m + \ldots + nxy^{n-1} + y^n$$

Here m designates the term in the expansion ($1 \le m \le n+1$).

D. Power Series Expansions

The Taylor series expansion is the key

$$f(x) = f(x_0) + f'(x_0)(x-x_0) + \frac{f''(x_0)}{2!}(x-x_0)^2 + \frac{f^{(3)}(x_0)}{3!}(x-x_0)^3 + \ldots$$

where $f'(x_0)$, $f''(x_0)$, $f^{(3)}(x_0)$ are the 1^{st}, 2^{nd}, and 3^{rd} derivatives of $f(x)$ evaluated at $x = x_0$. When the expansion is about $x = 0$, this reduces to the Maclaurin series

$$f(x) = f(0) + f'(0)x + \frac{f''(0)}{2!}x^2 + \frac{f^{(3)}(0)}{3!}x^3 + \ldots$$

Special cases are

$$\begin{aligned} \exp(ax) &= 1 + ax + \frac{a^2x^2}{2} + \frac{a^3x^3}{6} + \ldots \\ \frac{1}{1 \pm ax} &= 1 \mp ax + a^2x^2 \mp a^3x^3 \\ \ln(1 \pm x) &= \pm x - \frac{x^2}{2} \pm \frac{x^3}{3} + \ldots \end{aligned}$$

E. Roots of Functions

Before graphing calculators were available, there were many analytic methods (such as the Newton-Raphson method) for finding roots of functions — the values of x where $f(x) = 0$. Now, with mathematical software this is far easier. I will give you an example with Matlab.

Suppose you wish to find the root of $f(x) = 4x^3 - 8.72x^2 + 8.72x - 2.18$, where you know that

x must lie in the range $0 \leq x \leq 0.5$.

Here's the matlab script

```
syms x; f=4*x3̂-8.72*x2̂+8.72*x-2.18;
```

II. TRANSITIONS BETWEEN ENERGY LEVELS AND SPECTROSCOPY

Consider a transition from an initial level 'i' to a final level 'f'. The energy difference is $\Delta\mathcal{E}_{if} = \mathcal{E}_f - \mathcal{E}_i$, where the subscripts '$f$' and '$i$' designate the final and initial energies. The Bohr equation relates $\Delta\mathcal{E}_{if}$ to the frequency of the light that will cause this transition to occur, namely

$$\Delta\mathcal{E}_{if} = h\nu = hc/\lambda$$

Here we have used the relation between the frequency and the wavelength of light ($\lambda\nu = c$ where c is the speed of light). If we further define the "wavenumber" $\tilde{\nu} = 1/\lambda$, (*note (10/1/16) to be consistent with the text we are using* $\tilde{\nu}$ *to designate* $1/\lambda$) we have

$$\Delta\mathcal{E}_{if} = hc\tilde{\nu}$$

or

$$\tilde{\nu} = \Delta\mathcal{E}_{if}/hc \tag{1}$$

Let us use a diatomic molecule as an example. The vibrational energies are given by

$$\mathcal{E}_n = (n + 1/2)h\nu_v = (n + 1/2)hc\tilde{\nu}_v \tag{2}$$

where the vibrational frequency is defined by $\nu_v = (1/2\pi)\sqrt{k/\mu}$ with k being the force constant and μ being the reduced mass of the diatomic. This is the circular frequency of the vibration. The angular frequency ω_v is 2π times the angular frequency; in other words $\omega_v = \sqrt{k/\mu}$. I will use n to designate the vibrational quantum number (n=0, 1, 2, ...) instead of v, because the italic-'vee' (v) is too easy to confuse with 'nu' (ν). I have added the subscript 'vee' to the frequencies ν_v and ω_v to distinguish them from the circular and angular frequencies of light. Note that h and $\hbar$ have units of J·s and ν_v and ω_v have units of sec^{-1}, so that $h\nu_v$ and $\hbar\omega_v$ have units of energy. In the third term in Eq. (2) I have introduced the vibrational wavenumber, which I will call $\tilde{\nu}_v$. The units of $\tilde{\nu}_v$

is 1/length. The book calls $\tilde{\nu}_v$ the "fundamental vibrational frequency" (Tab. 1.4) even thought this quantity does *not* have units of frequency.

Now, for a transition from vibrational level n to level $n+1$, $\Delta\mathcal{E}_{if} = h\nu_v = hc\tilde{\nu}_v$, so that Eq. (1) becomes

$$\tilde{\nu}_{n\to n+1} = \frac{h\nu_v}{hc} = \tilde{\nu}_v$$

Consider now rotations (*changed, 10/1/2016*). The text (McQuarrie and Simon) give a non-standard definition of the rotational constant. This will be compared here with the standard definition. For a diatomic molecule, the rotational energies are given by

$$\mathcal{E}_J = \frac{\hbar^2}{2\mu r^2}J(J+1) = \frac{\hbar^2}{2I}J(J+1) \tag{3}$$

where I is the moment of inertia ($I = \mu r^2$) and μ is the reduced mass of the molecule. The energy gap for a transition out of rotational level J into rotational level $J+1$ is

$$\Delta E_{J\to J+1} = \mathcal{E}_{J+1} - \mathcal{E}_J = \frac{\hbar^2}{2I}2(J+1)$$

This we can write as

$$\begin{aligned} \Delta E_{J\to J+1} &= 2B(J+1)\,(\text{standard definition}) \\ &= 2h\mathcal{B}(J+1)\,(\text{McQuarrie}-\text{Simon definition}) \end{aligned} \tag{4}$$

In both cases, the constants B and $\mathcal{B}$ are called the "rotational constant". Note that the units of B (the standard rotational) are energy (J), while the units of $\mathcal{B}$ (the McQuarrie-Simon rotational constant) are frequency (s^{-1}).

Because $\Delta E = h\nu$, or $\nu = \Delta E/h$, we see from Eq. (4) that for the $J \to J+1$ transition

$$\nu_{J\to J+1} = \frac{2}{h}B(J+1) = 2\mathcal{B}(J+1)$$

Since the wavenumber of the transition is $\tilde{\nu} = 1/\lambda = \nu/c$, we find

$$\tilde{\nu}_{J\to J+1} = \frac{2}{hc}B(J+1) = \frac{2}{c}\mathcal{B}(J+1)$$

In both the standard and McQuarrie-Simon definition we express the wavenumber for the $J \to J+1$ transition in terms of a rotational constant in wavenumber (s^{-1}) units, $\tilde{B}$.

$$\tilde{\nu}_{J\to J+1} = 2\tilde{B}(J+1)$$

Thus, in terms of either B or $\mathcal{B}$

$$\tilde{B} = \frac{B}{hc} = \frac{\mathcal{B}}{c}$$

III. CRITICAL POINT OF A VAN DER WAAL'S GAS

The van der Waals equation of state is

$$P = \frac{RT}{\bar{V}-b} - \frac{a}{\bar{V}^2} \tag{5}$$

At the critical temperature, there occurs an inflection point on the isotherm (the plot of P as a function of V). An inflection point is a point where both the first and second derivatives vanish, namely

$$\left(\frac{\partial P}{\partial \bar{V}}\right)_{T=T_C} = \left(\frac{\partial^2 P}{\partial \bar{V}^2}\right)_{T=T_C} = 0$$

Differentiation of Eq. (5) gives (you should check these results)

$$\frac{\partial P}{\partial V} = -\frac{RT}{(\bar{V}-b)^2} + \frac{2a}{\bar{V}^3}$$

or

$$(\bar{V}-b)^2 = \frac{RT}{2a}\bar{V}^3 \tag{6}$$

Similarly, setting $(\partial^2 P/\partial V^2)$ equal to 0 and rearranging gives (again, you should check these results)

$$(\bar{V}-b)^3 = \frac{RT}{3a}\bar{V}^4 \tag{7}$$

We can divide Eq. (7) by Eq. (6) to get

$$(\bar{V}-b)=\frac{2a}{3a}\bar{V}=\frac{2}{3}\bar{V}$$

which can be solved to give

$$\bar{V}_C=3b$$

A student didn't like dividing 0 by 0, so here's an alternate solution: Multiply Eq. (6) by $(\bar{V}-b)$, to obtain

$$(\bar{V}-b)^3=\frac{RT}{2a}\bar{V}^3(\bar{V}-b)$$

Now, since the left-hand-side (l.h.s) of this equation is to the l.h.s. of Eq. (7), we can set the two r.h.s's equal, to obtain

$$\frac{RT}{2a}\bar{V}^3(\bar{V}-b)=\frac{RT}{3a}\bar{V}^4$$

This can be simplified to give

$$\bar{V}_C=3b$$

Note that we have added a subscript C to indicate that this relation holds only at the critical point.

Now, you can substitute this expression for V_C into Eq. (6) to obtain an expression for T_C, namely

$$T_C=\frac{8a}{27bR}$$

Finally, substituting the expressions for V_C and T_C into the van der Waals equation of state gives (*corrected 9/14/2014*)

$$P_C=\frac{a}{27b^2}$$

IV. BOLTZMANN DISTRIBUTION AND SUMMATION; INDEPENDENCE OF ZERO OF ENERGY

Boltzmann postulated that at equilibrium the population in level j is proportional to its energy

$$n_j \sim \exp(-E_j/kT)$$

The total population is $N = \sum_j n_j$. We'll assume here that $j = 1$ corresponds to the lowest level. The relative (or fractional) population in each level is

$$p_j = n_j/N = \exp(-E_j/kT)/\sum_j \exp(-E_j/kT) \tag{8}$$

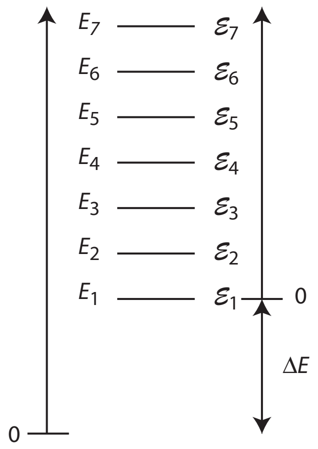
This quantity p_j is also the probability that level j will be occupied. The sum of all the probabilities is, of course, equal to 1.

$$\sum_j p_j = 1$$

Now, suppose we define the zero of energy as the energy of the lowest level. Then for each level j, the original energies are defined in terms of the energies with respect to the new zero of energy (the $\mathcal{E}_j$; see the figure below) as

$$E_j = \mathcal{E}_j + \Delta E$$

Now, in terms of the $\mathcal{E}_j$, the fractional populations of Eq. (8) are



$$p_j = n_j/N = \exp[-(\mathcal{E}_j + \Delta E)/kT]/\sum_j \exp[-(\mathcal{E}_j + \Delta E)/kT]$$

Because $\exp(a+b) = \exp(a)\exp(b)$, we can get rid of the constant factor of $\exp(-\Delta E/kT)$, to obtain (I'm counting on you to show this!)

$$\begin{aligned} p_j &= n_j/N \exp[-(\mathcal{E}_j + \Delta E)/kT]/\sum_j \exp[-(\mathcal{E}_j + \Delta E)/kT] \\ &= \exp(-\Delta E/kT)\exp(-\mathcal{E}_j/kT)/\sum_j \exp(-\Delta E/kT)\exp(-\mathcal{E}_j/kT) \\ &= \exp(-\mathcal{E}_j/kT)/\sum_j \exp(-\mathcal{E}_j/kT) \end{aligned}$$

We can compare this equation with Eq. (8), namely

$$p_j = n_j/N = \exp(-E_j/kT)/\sum_j \exp(-E_j/kT) = \exp(-\mathcal{E}_j/kT)/\sum_j \exp(-\mathcal{E}_j/kT)$$

in other words, the probability that level j is occupied is independent of our arbitrary choice of the zero of energy!

The quantity $\sum_j \exp(-\mathcal{E}_j/kT)$ is designated the "partition function" (often denoted by the letter q) and is the total population (or the total number of states) at temperature T. Thus, the probability that the system is in level j is

$$p_j = \frac{1}{q(T)} \exp(-\mathcal{E}_j/kT)$$

Since $\mathcal{E}_1 = 0$ (with the shifted zero of energy), you can show that

$$\lim_{T\to 0} q(T) = 1$$

The partition function is sometimes denoted by the letter z (instead of q). Note that the letter q is also used to designate the heat (see Eq. 5.10 of McQuarrie and Simon; $\Delta U = q + w$) which you sometimes see in differential form as

$$dU = \delta Q + \delta W$$

V. RELATION BETWEEN PARTITION FUNCTION AND ENERGY

Let us differentiate the natural logarithm of q. We know that

$$\frac{d\ln[f(x)]}{dx} = \frac{1}{f(x)}\frac{df(x)}{dx}$$

You can also show that (do this yourself)

$$\frac{dq(T)}{dT} = \frac{1}{kT^2}\sum_j \mathcal{E}_j \exp(-\mathcal{E}_j/kT) \tag{9}$$

Thus,

$$\frac{d\ln[q(T)]}{dT} = \frac{1}{q(T)}\frac{1}{kT^2}\sum_j \mathcal{E}_j \exp(-\mathcal{E}_j/kT) \tag{10}$$

But the average energy $\langle\mathcal{E}\rangle$ is (by definition the average value of any quantity is the sum over all levels of the property in each level multiplied by the probability for that level)

$$\langle\mathcal{E}\rangle = \sum_j p_j \mathcal{E}_j$$

So you can show that

$$\frac{d\ln[q(T)]}{dT} = \frac{1}{kT^2}\langle\mathcal{E}\rangle$$

or

$$\langle\mathcal{E}\rangle = kT^2\frac{d\ln[q(T)]}{dT} \tag{11}$$

This is dimensionally correct. The partition function is dimensionless, as is its logarithm. Consequently, the derivative of $\ln(q)$ with respect to temperature has units of $1/T$, so that the quantity

$$kT^2\frac{d\ln[q(T)]}{dT}$$

has units of kT, which is energy. Thus (happily for us) the units of the left hand side and the right hand side are the same!

It is perhaps simpler to differentiate first with respect to β. Since

$$q = \sum_j \exp(-\varepsilon_j \beta)$$

then

$$\frac{d \ln q}{d\beta} = -\frac{1}{q} \sum_j \varepsilon_j \exp(-\varepsilon_j \beta) = -\langle \mathcal{E} \rangle \tag{12}$$

Now, since $\beta = 1/kT$ or $T = 1/k\beta$, application of the chain rule gives

$$\frac{d}{d\beta} = \frac{d}{dT}\frac{dT}{d\beta} = -\frac{1}{k\beta^2}\frac{d}{dT} = -kT^2 \frac{d}{dT}$$

Thus, from Eq. (12) we obtain Eq. (11).

VI. PARTITION FUNCTION OF AN IDEAL GAS

The energy levels of a particle in a cubic box of length a are

$$E_{n_x,n_y,n_z} = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right) = A\left(n_x^2 + n_y^2 + n_z^2\right)$$

where $A = h^2/(8ma^2)$. The partition function for translation is then

$$q_t = \sum_{n_x}\sum_{n_y}\sum_{n_z} \exp[-A(n_x^2 + n_y^2 + n_z^2)\beta]$$

but, since $\exp(a+b) = \exp(a)\exp(b)$, we have

$$q_t = \sum_{n_x} \exp(-An_x^2\beta) \sum_{n_y} \exp(-An_y^2\beta) \sum_{n_z} \exp(-An_z^2\beta)$$

Each one of these three terms is identical, except that the summation is over a different index, so we can write

$$q_t = \left[\sum_n \exp(-An^2\beta)\right]^3$$

Now, since the summation involves very large values of n, we can replace the summation by an integral and obtain

$$q_t \approx \left[\int_1^\infty \exp(-An^2\beta)dn\right]^3 \approx \left[\int_0^\infty \exp(-An^2\beta)dn\right]^3$$

Since there are so many values of n that contribute we have replaced the lower limit by $n = 0$ (instead of $n = 1$) without loss of accuracy Now, since

$$\int_0^\infty \exp(-x^2)dx = \frac{\pi^{1/2}}{2}$$

we can do the variable substitution $x^2 = An^2\beta$ so that $x = n(A\beta)^{1/2}$ and $dn = (A\beta)^{-1/2}dx$ with the result

$$\int_0^\infty \exp(-An^2\beta)dn = \left(\frac{\pi}{4A\beta}\right)^{1/2}$$

Use a table of integrals or Wolfram Alpha with the command `‘integral(exp(-a*x^2)x^2) from 0 to infinity’` to verify this result.

Thus, you can show that

$$\lim_{n\to large} q_t = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V$$

VII. MAXWELL-BOLTZMANN SPEED DISTRIBUTION

In classical mechanics, all energy levels are allowed. A particle's motion is defined by its position and velocity $\vec{v}$. The kinetic energy of the particle is $E^{(kin)} = \frac{1}{2}ms^2$, where s is the speed

$$s = |\vec{v}| = (v_x^2 + v_y^2 + v_z^2)^{1/2} \tag{13}$$

In quantum mechanics, we know that the partition function is a sum over all allowed energy levels weighted by the degeneracy and the exponential of the energy multiplied by β. In a classical description, the partition function is the integral over a distribution function,

$$q_t(s;\beta) = g(s)\exp[-E^{(kin)}(s)\beta]$$

where $g(s)$ is the number of orientations of $\vec{v}$ for which $\vec{v} = s$. Here, the distribution function depends parametrically on β (and, hence, parametrically, on the temperature T). This is indicated by the semicolon in the argument of q_t.

The degeneracy $g(s)$ is the number of ways we can have $\vec{v}_x$, $\vec{v}_y$ and $\vec{v}_z$ so that the magnitude of the velocity is s. This is just the area of a sphere of radius s, namely $4\pi s^2$. We are integrating over the surface of a sphere in velocity space of radius s. To normalize the so-called "velocity" distribution (in reality, it is a speed distribution), we require that

$$\int_0^\infty q_t(s;\beta)ds = 1$$

Knowing that $\int_0^\infty x^2 \exp(-\alpha x^2)dx = \sqrt{\pi}/(4\alpha^{3/2})$, you can obtain the following expression for the normalized "Maxwell-Boltzmann" speed distribution.

$$q_t(s;\beta) = \left(\frac{2\beta^3 m^3}{\pi}\right)^{1/2} s^2 \exp(-\tfrac{1}{2}ms^2\beta) = \left(\frac{2m^3}{\pi(kT)^3}\right)^{1/2} s^2 \exp(-\tfrac{1}{2}ms^2/kT) \tag{14}$$

Note that this is equivalent to

$$q_t(s;\beta) = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} s^2 \exp(-\tfrac{1}{2}ms^2/kT) \tag{15}$$

an expression you often see. From either of these equations you can show that the average speed $\langle s\rangle$ is

$$\langle s\rangle = \int_0^\infty s\, q_t(s;\beta)ds = \left(\frac{8kT}{\pi m}\right)^{1/2}$$

an important result worth remembering. Similarly, you can show that the average value of s^2 is

$$\langle s^2\rangle = \int_0^\infty s^2\, q_t(s;\beta)ds = \frac{3kT}{m}$$

This implies that the average kinetic energy is

$$\langle KE\rangle = \frac{1}{2}m\langle s^2\rangle = \frac{3}{2}kT$$

which is identical to the result obtained for the average energy of the particle in a box. The standard deviation of the velocity (the square root of the variance) is

$$\left(\langle s^2\rangle - \langle s\rangle^2\right)^{1/2} = (3-8/\pi)^{1/2}(kT/m)^{1/2} \approx 0.67(kT/m)^{1/2}$$

Finally, the most-probable speed (the values of s for which $q_t(s)$ is a maximum, can be obtained by differentiating $q_t(s)$ with respect to s, and setting this to zero. We find

$$s_{mp} = \left(\frac{2kT}{m}\right)^{1/2}$$

VIII. BOILING AND MELTING OF WATER AND THE HYDROGEN BOND

For water the temperatures of fusion and vaporization, and their associated enthalpies at 1 bar pressure are given in Table I. In ice there are 4 hydrogen bonds per water molecule. In the gas phase there are no hydrogen bonds. Therefore, if we could calculate the *energy* (ΔU) of sublimation, and divide this number by 4, we would obtain an estimate of the strength of a hydrogen bond. The energy of a phase change ($\alpha \to \beta$) is given in terms of the enthalphy of the phase change by the relation

TABLE I: Reference thermodynamic properties of water in its three phases.

Property	$H_2O(s)$	$H_2O(l)$	$H_2O(g)$
$T_{\text{transition}}(K)$	$273.15 (s \to l)$	$373.15\ (l \to g)$	
$\Delta H_{\text{transition}}(\text{kJ/mol})$	6.029 $(s \to l)$ (0.0 C)	40.657 $(l \to g)$ (100 C)	
$\Delta H_f^{(o)}(\text{kJ/mol})$	–292.6	–286.63	–241.58
$G^{(o)}(\text{kJ/mol})$	–236.59	–237.18	–228.59
$S^{(o)}(\text{kJ/mol} \cdot \text{K})$	41.8	69.91	188.7
$C_p(\text{J/mol} \cdot \text{K})$	37.8 K	75.3 (25°C)	37.47 (100°C)
ρ(at melting point)(kg/m^3)	916.72	999.84	$\bar{V} = RT/P$

$$\Delta U_{\alpha\to\beta} = \Delta H_{\alpha\to\beta} - \Delta(PV)_{\alpha\to\beta}$$

We assume constant pressure, so $\Delta(PV) = P\Delta V$. So, $\Delta U_{fus} = \Delta H_{fus} - 1\text{atm} \times (\bar{V}_l - \bar{V}_s)$. We know that

$$V_l - V_s = M(1/\rho_l - 1/\rho_s) = 0.018(1/999 - 1/916) = 1.63 \cdot 10^{-5} m^3/mol$$

Here M is the molar mass (1.8e-4 kg/mol). The volume correction makes a negligibly small correction, so $\Delta U_{fus} \approx \Delta H_{fus} = \Delta H_f^{(o)}(l) - \Delta H_f^{(o)}(s) = 6.00kJ/mol$.

For vaporization, the volume correction is larger, since $V_g = RT/P = 0.0307m^3$ at $T = 373$ K. So,

$$\Delta U_{vap} = \Delta H_{vap} - 1.01 \cdot 10^5 \times 0.0307 = \Delta H_{vap} - 3100J = 40.657 - 3.1 = 37.56$$

Summing these energies gives

$$\Delta U_{sub} \approx \Delta U_{fus} + \Delta U_{vap} = 6.00 + 37.56 = 42.56J/mol$$

Dividing by 4 gives the average energy of a H-bond (11.02 = 42.56/4)

For fusion, we have seen that $\Delta U_{fus} = 6.00$ kJ/mol. To melt ice, then, we need to add energy roughly equivalent to 0.5 H bonds. Therefore, when ice melts approximately 1/2 an H-bond is broken.

IX. PRESSURE AND THE PARTITION FUNCTION

We will use kinetic theory to demonstrate the relationship between the pressure and the partition function

$$P = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{N,T}$$

Here we have used upper-case Q, which represents the total partition function for a system consisting of N atoms (or molecules).

Consider a particle moving with speed v in a cubic box of length a. The momentum of the particle is mv. For simplicity let's assume that the particle is moving perpendicular to one of the faces of the box. When the particle collides with a face, the force exerted on the wall is equal to the change in momentum. This is $\Delta p = 2mv$. The factor of two arises because the momemtum changes from $+mv$ to $-mv$, or vice versa. The number of collisions in unit time with the face is v/a. Thus, the force exerted on the wall in unit time is $2mv^2/a$. The area of the wall is a^2, so that the pressure (the force per unit area) is $P = 2mv^2/a^3 = 2mv^2/V$ where V is the volume.

Now, the kinetic energy of the gas is $E^{(kin)} = \frac{1}{2}mv^2$. So the preceding result is $P = 4E^{(kin)}/V$. This is an overestimate, since, on average, the molecule can be moving in the $+x$, $-x$, $+y$, $-y$, $+z$, or $-z$ direction. Thus the pressure on any particular face is $4E^{(kin)}/V$ divided by 6, or, finally

$$P = \frac{2E^{(kin)}}{3V} \tag{16}$$

Now, for a particle in a box all the energy is kinetic (we assume the potential energy is zero inside the box)

$$E_j = E_j^{(kin)} = E_{n_x,n_y,n_z} = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right) = \frac{h^2}{8mV^{2/3}}\left(n_x^2 + n_y^2 + n_z^2\right)$$

Thus, you can show using Eq. (16) that the contribution to the pressure due to a particle in energy level E_j is (call this contribution P_j)

$$P_j = \frac{2E_j^{(kin)}}{3V} = -\frac{\partial E_j}{\partial V} \tag{17}$$

So, the average pressure, again due to collisions of a *single* atom or molecule with the walls of the container, is equal to the average of P_j, which we can calculate from the partition function q

$$\langle P \rangle = -\frac{1}{q}\sum_j \frac{\partial E_j}{\partial V}\exp(-E_j\beta) \tag{18}$$

The partial differentiation is with respect to volume with T held constant (equivalent to β held constant). From the definition of the partition function you can easily show that

$$\langle P \rangle = \frac{1}{\beta}\frac{\partial \ln q}{\partial V} = kT\frac{\partial \ln q}{\partial V} \tag{19}$$

In fact we have N molecules, so that $Q = q^N/N!$ Consequently, the average pressure exerted by N molecules is

$$\langle P \rangle = NkT\frac{\partial \ln q}{\partial V} = kT\frac{\partial \ln q^N}{\partial V} = kT\frac{\partial \ln Q}{\partial V} \tag{20}$$

X. ENTROPY OF A TWO-LEVEL SYSTEM

The relation between the partition function and the entropy is

$$\mathcal{S} = \frac{\langle \mathcal{E} \rangle}{T} + k \ln Q \tag{21}$$

Consider N non-interacting particles each described by a two-level system, where the particle can have energy $\pm\varepsilon$. An example might be N protons each of which can be in a nuclear spin state $+1/2$ or $-1/2$. Since $Q = q^N$ and $\langle \mathcal{E} \rangle = N\langle E \rangle$ (where E is the average energy of a single particle), we can write

$$\mathcal{S} = NS = N\left(\frac{\langle E \rangle}{T} + k \ln q\right)$$

The entropy is the sum of the entropies of the individual particles.

Let $x = \exp(-\varepsilon\beta)$. Then, as we have discussed in class, $q = 1/x + x = (1 + x^2)/x$, so that

$$\ln q = -\ln x + \ln(1 + x^2) = +\varepsilon\beta + \ln(1 + x^2)$$

or, using the known power series expansion $\ln(1 + z) = z - z^2/2 + \ldots$,

$$k \ln q = \frac{\varepsilon}{T} + k \ln(1 + x^2) = \frac{\varepsilon}{T} + k\left(x^2 - \frac{1}{2}x^4 + \cdots\right) \tag{22}$$

and

$$\langle E \rangle = -\frac{\partial \ln q}{\partial \beta} = -\frac{\partial \ln q}{\partial x}\frac{\partial x}{\partial \beta} = -\varepsilon\frac{1 - x^2}{1 + x^2} = -\varepsilon\left(1 - 2x^2 + 2x^4 + \cdots\right)$$

so that

$$\frac{\langle E \rangle}{T} = -\frac{\varepsilon}{T}\left(1 - 2x^2 + 2x^4 + \cdots\right) \tag{23}$$

Combining Eqs. (23) and (22) leads to

$$S = kx^2\left(1 + \frac{2\varepsilon}{kT}\right) + \mathcal{O}(x^4) + \cdots$$

A. Limiting behavior

Since $\lim_{T\to 0} x = 0$, we find

$$\lim_{T\to 0} S = 0$$

which is what we expect (see Sec. XI below). At high temperature, $x \to 1$ in which case we have

$$\lim_{T\to\infty} S = k \ln 2$$

At high temperature $W = 2$ (both levels are equally probable).

XI. GENERAL BEHAVIOR OF ENTROPY AS $T \to 0$

For any system with a non-degenerate ground state the partition function is

$$\begin{aligned} q &= \exp(-E_0\beta) + g_1 \exp(-E_1\beta) + g_1 \exp(-E_2\beta) + \ldots \\ &= \exp(-E_0\beta) \left[1 + g_1 \exp(-\Delta E_{10}\beta) + g_2 \exp(-\Delta E_{20}\beta) + \ldots\right] \end{aligned}$$

where $\Delta E_{j0} = E_j - E_0$ (note that this is always a positive number) and g_j designates the degeneracy of the j^{th} level. At low temperature

$$\exp(-\Delta E_{20}\beta) << \exp(-\Delta E_{10}\beta)$$

and, similarly, for all $\exp(-\Delta E_{j0}\beta)$ with $j > 2$. Consequently, we can retain only the first two terms

$$\lim_{T\to 0} q = \exp(-E_0\beta) \left[1 + g_1 \exp(-\Delta E_{10}\beta)\right] = \exp(-E_0\beta)(1 + g_1 x) \tag{24}$$

where we have defined $x = \exp(-\Delta E_{10}\beta)$. From this expression, we obtain

$$\lim_{T\to 0} \ln q = -E_0\beta + \ln(1 + g_1 x) \approx -E_0\beta + g_1 x + \mathcal{O}(x^2) \tag{25}$$

We know that the average energy is $\langle E\rangle = -\partial \ln q/\partial\beta$, so Using Eq. (25) we obtain

$$\lim_{T\to 0}\langle E\rangle = +E_0 - g_1\frac{\partial x}{\partial\beta} = E_0 + g_1\Delta E_{10}x$$

Insterting this result and Eq. (25) into the general expression for the entropy in terms of $\langle E\rangle$ and q [Eq. (21)], we obtain

$$\lim_{T\to 0} S \approx \frac{E_0}{T} + \frac{g_1\Delta E_{10}x}{T} - \frac{E_0}{T} + kg_1x = kg_1x\left[1 + \frac{\Delta E_{10}}{kT}\right]$$

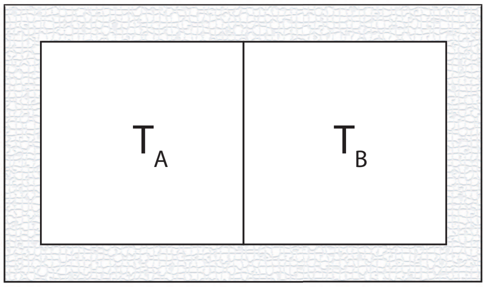
At low T, $x = \exp(-\Delta E_{10}/kT)$ goes to zero faster than its argument, $\Delta E_{10}/kT$, diverges. Thus, the entropy goes to zero at low T, regardless of the value of the energy gap ΔE_{10}. Consequently, for any system with a non-degenerate ground state, and regardless of how we chose the zero of energy (E_0) the entropy vanishes at $T = 0$, which is the Third Law.

XII. SPONTANTEOUS TRANSFORMATIONS AND APPROACH TO EQUILIBRIUM

In thermodynamics the determination of whether a transformation is spontaneous as well as the approach to equilibrium is governed by inequalities, involving the entropy and the the two free energies. I shall review these here.

A. Entropy

Consider a system where we have two equal volumes at different temperatures. Heat is allowed to flow slowly from one side to another. Since the system is isolated, the heat flow q_A from side A must equal the negative of the heat flow from side B, $q_A = -q_B$. The overall change in entropy is



thus

$$dS = \frac{\delta q_A}{T_A} + \frac{\delta q_B}{T_B} = \delta q_A \left(\frac{1}{T_A} - \frac{1}{T_B} \right)$$

We know that if $T_A > T_B$, then heat will flow out from side A ($\delta q_A < 0$). Thus dS will be positive. If the system is at equilibrium, then $dS = 0$. So dS is positive and gradually decreases to 0, at which point the two systems are in equilibrium, at the same temperature.

An isolated system that is not in equilibrium will evolve only in such a way that $dS > 0$. This is a statement of the Second Law.

In the case of a system which is not isolated, the most useful statement of the Second Law is

$$dS \geq \frac{\delta q}{T}$$

with the equality pertaining to a reversible process.

The isothermal expansion of an ideal gas at T_1 from V_1 to V_2 is the perfect illustration of this. The pressure decreases to $P_2 = (V_1/V_2)P_1$. In a reversible expansion $\delta q = -\delta w = PdV$. For an irreversible expansion $P_{ext} = P_2$, so that $\delta q = P_2 dV$. Since $P_2 \leq P$, $\delta q_{rev} > \delta q$. Thus dS will be $\geq \delta q/T$.

B. Helmholz free energy

The Helmholz free energy is defined as the state function

$$A = U - TS$$

The differential of A is then

$$dA = dU - TdS - SdT$$

For a transformation at constant temperature ($dT = 0$)

$$dA = dU - TdS \tag{26}$$

The First Law states $dU = \delta q + \delta w$. Thus

$$dA = \delta q - TdS + \delta w \tag{27}$$

We also know from Subsection XII A that $dS \geq \delta q/T$ or $TdS > \delta q$ (since the temperature is always positive, the sense of the inequality is not changed when we multiply up by T). We can also write this inequality as $\delta q - TdS \leq 0$. Combining this with Eq. (27) gives

$$dA - \delta w \leq 0 \tag{28}$$

The equality applies for a reversible process There are several consequences of Eq. (28):

1. The change in the Helmholz free energy is equal to the reversible work that accompanies a transformation.

2. If only PV work is allowed, at constant volume $\delta w = 0$. Thus at constant volume [and constant temperature, the assumption made in deriving Eq. (26)], a reversible transformation is characterized by $dA = 0$. Also, a transformation will occur spontaneously only if $dA < 0$. Note that

    (a) The "less than (irreversible) or equal (reversible)" sign here arises because of the 2nd law [$\delta q - TdS \leq 0$, see immediately before Eq (28)]

    (b) $\delta w = -PdV$, for an infinitesimal transform. The differences between reversible and irreversible work comes only when we specify the dependence of P on the path, so that
    $w_{rev} = \oint PdV$ or
    $w_{irrev} = -P_{ext} \oint dV = -P_{ext}\Delta V$.

C. Gibbs free energy

We define the Gibbs free energy as the state function $G = H - TS$. The differential is

$$dG = dH - TdS - SdT$$

For a transformation at constant temperature, this becomes

$$dG = dH - TdS \tag{29}$$

Knowing that $dH = dU + PdV + VdP = \delta q + \delta w + PdV + VdP$. Remembering (2nd law) that $\delta q - TdS \leq 0$, we can write this as

$$dG - (\delta w + PdV) - VdP \leq 0$$

Suppose we keep the pressure constant, then

$$dG - (\delta w + PdV) \leq 0$$

Just as in the case of the Helmholz free energy, there are several consequences to this inequality

1. The total work is the sum of PV work and non-PV work δ_w^{nPV} (electrical work, for example). In the case of a reversible transformation $\delta w_{rev} = -PdV + \delta w_{rev}^{nPV}$. Consequently

   $$dG \leq \delta w_{rev}^{nPV}$$

   Thus, the change in the Gibbs free energy is a measure of the non-PV work that can be extracted from the transformation. This, obviously, will be of particular importance in the study of batteries and fuel cells.

2. If there is no non-PV work, then for a spontaneous process at constant temperature and constant pressure the change in the Gibbs free energy will be < 0. G will decrease until equilibrium is reached, at which point dG will equal zero.

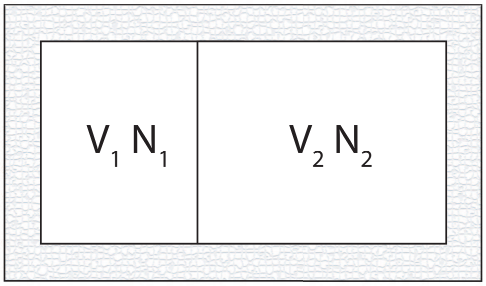
D. Gibb's Paradox

Consider a large volume, containing gas molecules of a single species, partitioned into volumes V_1 and V_2. The number densities in each partition are identical, so that

$$V = V_1 + V_2;\ N = N_1 + N_2;\ \text{and}\, N/V = N_1/V_1 = N_2/V_2$$

The total entropy is $S = S_1 + S_2$, where

$$S = k \ln Q + \frac{\langle E \rangle}{T}$$



If the gases are ideal then $Q = q^N$, where

$$q = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V$$

Thus (error corrected in red, 11/20/17 and magenta 11/13/19)

$$S_1 = \frac{\langle E_1 \rangle}{T} + N_1 k \ln q = \frac{\langle E_1 \rangle}{T} + N_1 k \left[C(T) + \ln V_1\right] \tag{30}$$

where $C(T) = \frac{3}{2}\ln(2\pi mkT/h^2)$ (note that C is independent of the volume). If we assume a monatomic gas, then $\langle E_1 \rangle = 3N_1kT$, so

$$S_1/k = N_1\left[C(T) + \ln V_1 + 3/2\right] \tag{31}$$

You can obtain a similar expression for S_2 and S.

Suppose you remove the partition. Then the entropy change is

$$\begin{aligned} \Delta S/k \quad &= (S - S_1 - S_2)/k = (3/2)[N - N_1 - N_2] + C(T)[N - N_1 - N_2] + [N \ln V - N_1 \ln V_1 - N_2 \ln V_2] \\ &= (N_1 + N_2)\ln(V_1 + V_2) - N_1 \ln V_1 - N_2 \ln V_2 = N_1 \ln V/V_1 + N_2 \ln V/V_2 \end{aligned}$$

Note that the $(3/2)kT$ and $C(T)$ terms cancel out. Since $V \geq V_1$ and $V \geq V_2$, the conclusion is that $\Delta S > 0$, regardless of the particular values of N_1 and N_2. This is Gibb's paradox. Why does the entropy increase when the partition is removed?

The answer lies in our neglect of particle indistinguishability. In fact

$$Q = \frac{q^N}{N!}$$

so that Eq. (31) becomes (we use Stirling's approximation)

$$S_1/k = N_1 \left[C(T) + \ln V_1 + \frac{3}{2} - \ln N_1 + 1 \right]$$

with a similar expression for S_2. And, also,

$$\begin{aligned} S/k &= N \left[C(T) + \ln V + \frac{3}{2} - \ln N + 1 \right] \\ &= (N_1 + N_2) \left[C(T) + \ln(V_1 + V_2) + \frac{3}{2} - \ln(N_1 + N_2) + 1 \right] \end{aligned}$$

You can then show that if the particles are treated as *indistinguishable*

$$\Delta S/k = (N_1 \ln V/V_1 + N_2 \ln V/V_2 - N_1 \ln N/N_1 - N_2 \ln N/N_2)$$

Now, because the number densities of both partitions are identical, $V/V_1 = N/N_1$ and $V/V_2 = N/N_2$, so that $\Delta S = 0$, which is what we expect.

This is consistent with the essential quantum hypothesis that identical particles are indistinguishable. Note that if the particles are *indistinguishable* then if we take the partition out and then put it back in at some later time, the ensemble is identical to what we had initially. What happens if the particles are distinguishable (suppose the particles in the left hand partition are labelled "red" and the in the right partion, "blue". Then, if we remove the partition, some of the red particles will move to the right and some of the blue particles, to the left. If we then put the partition back in, there will be more disorder than we had initially (hence a greater entropy).

XIII. BOILING OF WATER

Consider the boiling of water

$$\mathrm{H_2O}(l) \leftrightarrow \mathrm{H_2O}(g) \tag{32}$$

For this reaction, if we examine standard thermodynamics tables (see, for example, Table I above or the NIST webbook) we find, as we would expect

- the entropy of water vapor is significantly larger than that of the liquid (the vapor phase is much more disordered)
- the enthalpy of the liquid phase is significantly lower than that of the gas phase, because

each water molecule is more tightly bound to its neighbors in the liquid, where the molecule-molecule spacings are smaller

Thus, at 298 K, the free energy change for the liquid→vapor transformation [Eq. (32)] is $\Delta G_R = +8.59$ kJ, so that the transformation is not spontaneous. At a pressure of 1 bar (which is understood in the superscript "o") water will not boil at 298 K.

For a transformation $A \rightarrow B$ the equilibrium constant K_P can be written as [this is covered in Chap. 12, Eq. (12.11) of McQuarrie and Simon, which we unfortunately we may not cover this semester]

$$\ln K_P = -\Delta G_R / RT$$

At T=298, we obtain

$$\ln K_P = -8.59 \times 10^3/(8.314 \times 298) = -3.47 \tag{33}$$

or, equivalently

$$K_P = e^{-3.47} = 0.031$$

which is a small number. For a liquid in equilibrium with its vapor, the ratio of the pressure of the component in the vapor phase to the total pressure is

$$\frac{P_{\mathrm{H_20}}}{P^o} = K_P$$

Thus, we predict that at 298 K the vapor pressure of H_2O should be 0.0311 bar ≅ 23.6 torr. This estimate agrees extremely well with the measured value of 23.8 torr.

Similarly, you would predict that at an external pressure of 23.8 torr (0.0311 atm) water will boil at 298 K. If you lower the pressure enough, water will boil at room temperature. Hence, the unlucky astronaut who develops a pressure leak will end up exploding all over his space ship when the pressure drops to 0.0313 atm.

Now, let's see if we can use thermodynamics to predict the boiling point of water at a pressure of 1 atm. If we increase the temperature at a constant pressure, the Gibbs-Helmholtz equation (8.61) tells us that

$$\frac{d \ln K_P}{dT} = \frac{\Delta H_R^o}{RT^2}$$

so that

$$\begin{aligned}\ln K_P(T) &= \ln K_P(T=298) + \frac{\Delta H_R^o}{R}\int_{298}^{T}\frac{dT}{T^2} \\ &= \ln K_P(T=298) + \frac{\Delta H_R^o}{R}\left[-\left(\frac{1}{T}\right)\Big|_{298}^{T}\right] \qquad (34)\end{aligned}$$

At the boiling point, $P_{\mathrm{H}_2 0} = 1$ bar, so that

$$\ln K_P(T_b) = 0$$

This fact will allow us to use Eq. (1) to predict the boiling point of water. We have

$$0 = \ln K_P(T=298) + \frac{\Delta H_R^o}{R}\left(\frac{1}{298} - \frac{1}{T_b}\right)$$

From Table I, we see that $\Delta H_R^{(o)} = -241.58 + 286.63 = 45.05$ kJ/mol. Substituting this into the previous equation gives [remember Eq. (33)]

$$0 = -3.47 + \frac{4.51\times 10^4}{8.314}\left(3.3557\times 10^{-3} - \frac{1}{T_b}\right) \qquad (35)$$

The solution to this equation is

$$T_b = 368.4,$$

which is within 2% of the true boiling point of water.

Why is it in error? Because we are assuming that the enthalpy difference (ΔH_R) is constant over between 298 and 373 K. In fact [Eq. (4.18)]

$$\Delta H(373) = \Delta H(298) + \int_{298}^{T} \Delta C_p dT = 45.1 \times 10^3 + (37.47 - 75.3)(373 - 298) = 4.0865 \times 10^3$$

Let's assume that over the range $298 < T < 373$ the enthalpy change is approximately equal to the average of the values at T=298 (4.510×10^3) and at T=373 (4.0865×10^3), namely 43.0 kJ/mol. If we use this value in Eq. (35),

$$0 = -3.47 + \frac{43.0 \times 10^3}{8.314} \left(3.3557 \times 10^{-3} - \frac{1}{T_b} \right)$$

we predict $T_b = 372.5$ K, nearly equal to the exact answer.

This demonstrates (a) how the free energy difference controls the position of equilibria and (b) how knowing the thermodynamic properties well at 298 K, and knowing how these properties change with temperature allows us to make fundamental predictions about the temperature of phase changes, a very important aspect of the world around us.

XIV. STATISTICAL MECHANICAL EXPRESSIONS FOR THE HELMHOLZ AND GIBBS FREE ENERGIES

We know that

$$S = \frac{\langle E \rangle}{T} + k \ln Q$$

If we assume that the thermodynamic state function U is the same as the statistical-mechanical average energy, then

$$A = U - TS = -kT \ln Q \tag{36}$$

Thus, the Helmholz free energy is (with a minus sign) the thermal energy (kT) weighted by the natural logarithm of the number of Boltzmann-weighted available states.

Substitution of Eqs. (20) and (36) into the expression for the Gibbs free energy

$$G = H - TS = U + PV - TS = A + PV$$

gives

$$G = kT\left(-\ln Q + V\frac{\partial \ln Q}{\partial V}\right)$$

XV. ELECTRICAL POTENTIAL, FIELD, AND WORK

Just like the force (a vector quantity) is defined as the gradient of a potential (a scalar quantity), the vector electric field $\vec{E}$ can be defined in terms of a scalar electrical potential ϕ

$$\vec{E} = -\nabla\phi \tag{37}$$

or, in one dimension

$$E = -\frac{d\phi}{dx} \tag{38}$$

The fundamental SI electric unit is the ampere (A), which is a unit of current flow. The unit of charge is the coulomb (C) which is an ampere-second (A·s). The units of electric potential is the *volt* (V). From Eq. (37) we see that the unit of electric field then must be V/m.

The electrical (non-PV) work done to move a charge q from a point i to a point f in a constant electric field ($\vec{E}$ independent of the coordinates) is

$$w = q\int_i^f \vec{E}\cdot d\vec{r} = q\int_i^f E dx = -q\int_i^f \frac{d\phi}{dx}dx = -q\left(\phi_f - \phi_i\right) = -q\Delta\phi\,, \tag{39}$$

Since work has units of J, we see that 1 J = 1 C·V = 1 A·s·V . Note that Eq. (39) describes the electrial work done by whatever device moves the charge. You have to be careful, because the charge of a particle can be both positive or negative (whereas a mass can only be positive).

Positively charged particles will move (if free to do so) towards regions of lower electric potential ($\Delta\phi < 0$). Since the units of electric potential are volts, lower electric potential is designated lower "voltage". Similarly, a negatively charged particle (an electron, for example) will move towards regions of higher voltage. In both these cases the work ($-q\Delta\phi$) is positive.

In contrast, to move a positive charge into to a position of higher voltage requires electrical work to be done against the field of the electric force ($w < 0$). This is equivalent to moving a mass against a force (pressure is force per unit area). Similarly, the work to transfer a negatively charged particle from a region of higher voltage to a region of lower voltage is negative.

In both these cases the definition of the sign of w is consistent with the chemists' definition. Work is done by the electrical device ($w < 0$) to move the charge. This is equivalent to the sign convention for PV work. When a piston expands against an external pressure, work is done by the engine against the surroundings ($w < 0$). The engine is equivalent to the electrical device.

Typically, electrical devices are rated by the current flow (I), rather than the total charge, with

$$I = \frac{dq}{dt}$$

which has units of A. Under the assumption that the electric field does not depend on time, differentiation of Eq. (39) with respect to time gives

$$P \equiv \frac{dw}{dt} = \frac{dq}{dt}\int_i^f \vec{E}\cdot d\vec{r} = I\int_i^f \vec{E}\cdot d\vec{r} = -I\Delta\phi \ , \tag{40}$$

where P is the power (with units of J/s or, equivalently A·V). [The SI unit of power (J/s) is designated a *watt* (W); not to be confused with the work]. The work done by an electrical device in which a current of positively charged particles flow at a rate I from higher to lower voltage is

$$w = \int P\,dt = -\Delta\phi\int I dt$$

Since $\Delta\phi$ is negative (positively charged particles flow from higher to lower voltage), w is positive. This implies that electrical work is done on the device.

Because the work is the time integral of the power, electrical work is often quantified by the units watts-seconds (or kilowatt-hours), rather than Joules, which would be more correct.

XVI. CHEMICAL EQUILIBRIUM

Consider a system with N gaseous components, with n_i indicating the number of moles of each component. The chemical potential of the i^{th} component is defined as $\mu_i = (\partial G/\partial n_i)_{T,P,n_j\neq n_i}$. We assume that all the species are linked by a chemical reaction (for the sake of example let this be ν_AA + ν_BB → ν_YY+ ν_ZZ). Then, the composition of the system can be written in terms of a single variable ξ, sometimes called an "advancement parameter", so that the number of moles of any species i is $n_i = n_{i0} \pm \nu_i\xi$, where the "+" sign is taken for products and the "–" sign for reactants. The independent variables are S, T, and ξ. The latter describes the composition of the mixture.

At constant P and T, ξ will vary until G reaches a minimum (within the allowable range of ξ). This minimum will correspond to the vanishing of the derivative of G, with respect to ξ with T and P held constant, namely

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \frac{\partial}{\partial \xi}\left[\sum_{i=1}^{N} \mu_i (n_{i0} \pm \nu_i \xi)\right] = \sum_{i=1}^{N} \pm \mu_i \nu_i = 0 \tag{41}$$

Now, let's assume that all species can be treated as ideal gasses, so that

$$G_i = G_i^o + n_i RT \ln(P_i/P_0) = n_i \left[\bar{G}_i^o + RT \ln(P_i/P_0)\right] \tag{42}$$

Here the superscript "o" means the thermodynamic standard state (P=1 atm and T=298 K). If we measure the pressure in atm, the chemical potential of each species is $\mu_i = \partial G_i/\partial n_i = \bar{G}_i^o + RT \ln P_i$, Then Eq. (41) becomes

$$\sum_{i=1}^{N} \pm \nu_i \bar{G}_i^o + RT \sum_{i=1}^{N} \pm \nu_i \ln P_i = 0$$

The first summation is what we have termed ΔG_r^o, the free energy of reaction, so this preceding equation can be written as $\Delta G_r^o + RT \ln K_P = 0$ or

$$RT \ln K_P = -\Delta G_r^o$$

which is sometimes also written as

$$K_P = \exp(-\Delta G_r^o/RT) \tag{43}$$

Here we have introduced the "equilibrium constant"

$$K_P = \frac{P_Y^{\nu_Y} P_Z^{\nu_Z}}{P_A^{\nu_A} P_B^{\nu_B}}$$

If the gases are ideal, then the partial pressure of each gas is given by Dalton's law:

$$P_i = X_i P = n_i P / \sum n_i$$

A. Example: $N_2O_4 \leftrightarrow 2NO_2$

Consider a situation where we start with a particular initial number of molecules of both species [say, for example $n_{N_2O_4} = n_0$ and NO_2=0 (no NO_2 present initially)]. How do we determine, at a given temperature and pressure, the number of moles (or mole fraction, or partial pressure) of each species present at equlibrium? The procedure is to calculate K_P in terms of ξ, and then solve Eq. (43) for the value of ξ at equilibrium. To set things up, it's easiest to use a table, as shown immediately below. The number of moles of each species, the mole fractions, and partial pressures are given in the table

Parameters for the study of $N_2O_4 \leftrightarrow 2NO_2$

species	n_i		X_i	P_i
	initial	at equilibrium		
NO_2	0	2ξ	$2\xi/(n_0+\xi)$	$2P\xi/(n_0+\xi)$
N_2O_4	n_0	$n_0-\xi$	$(n_0-\xi)/(n_0+\xi)$	$P(n_0-\xi)/(n_0+\xi)$

The expression for the equilibrium constant is then

$$K_P = \frac{{P_{NO_2}}^2}{P_{N_2O_4}} = \frac{(2P\xi)^2}{(n_0+\xi)^2} \times \frac{n_0+\xi}{P(n_0-\xi} = \frac{4P\xi^2}{{n_o}^2-\xi^2} \tag{44}$$

So, we first obtain the value of K_P from Eq. (43), then solve for ξ by solving the quadratic equation $\xi^2(4P+K_P) = n_o^2 K_P$ to give

$$\xi = n_o \left(\frac{K_P}{4P+K_P} \right)^{1/2}$$

From the NIST webbook, we find for the $N_2O_4 \to 2NO_2$ reaction:

- $\Delta_r H^o$= 70.8 kJ/mol
- $\Delta_r S^o$= 275 J/K·mol.

  This gives
- ΔG_r^o= –11.359 kJ/mol

Consequently, at T=298K, K_P=97.98. If n_o=1 and P=1 atm, then ξ=0.980. The reaction is nearly complete. If we increase the pressure, then ξ will decrease. The position of equilibrium will shift to the side of the N_2O_4 reactant, as predicted by le Chatelier's principle. This is shown in the left-hand panel of the Fig. 1 below.

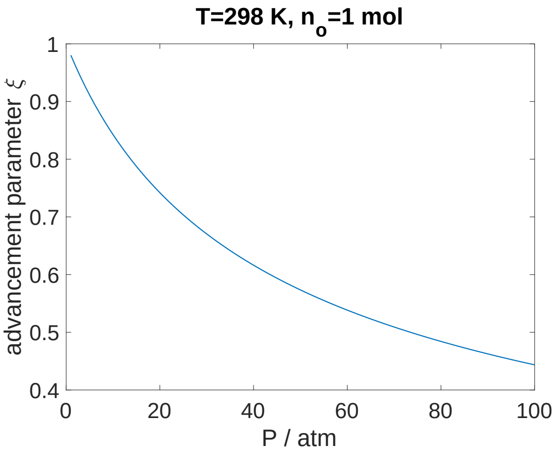


FIG. 1: N_2O_4 ↔$2NO_2$ equilibrium. Left panel: Pressure dependence of the advancement parameter ξ at T=298 K. Right panel: Temperature dependence of ξ at P=1 atm.

Now, the reaction is endothermic, since we're breaking the N_2O—N_2O bond. Le Chatelier's principle would predict that the equilibrium will shift to the left with increasing temperature. *For an endothermic reaction, heat is a reactant. Thus, increasing the heat will shift the equilibrium to the product side.* Let's see what we would predict from thermodynamics? We can still use Eq. (43), except that the free energy of reaction should be at a variable temperature T.

We know that $\partial G/\partial T = -S$. This will apply also to $\Delta_r G^T$. Thus

$$\Delta_r G^T = \Delta_r G^o - \int_{298}^{T} \Delta S_r(T) dT$$

Let's assume that the entropy of reaction is independent of temperature. Then

$$\int_{298}^{T} \Delta S_r(T) dT \approx \Delta S_r^o (T - 298)$$

So

$$K_P(T) = \exp(-\Delta_r G^T/RT) = \exp(-\Delta_r G^o/RT) \exp[+\Delta S_r^o (T - 298)/RT]$$

For each different temperature, we can obtain the appropriate value of ξ by solving Eq. (44).