Homework #8
Solutions

Schroeder 5.29, 5.30, 5.31, 5.32, 5.41, 5.76, 5.81, 5.82, 5.84

Carter 9.8, 10.2

Additional Problem :

Carter

9.8 a. The new temperature is the same as the old temperature, since internal energy of the system is conserved & the gases are ideal

$\boxed{(300K)}$

$$P_f = \frac{(n_1+n_2)RT}{V_1+V_2} = \frac{n_1+n_2}{2V}RT \quad \text{where } V_1=V_2=V$$

$$P_f = \frac{1}{2}\frac{n_1RT}{V} + \frac{1}{2}\frac{n_2RT}{V} = \frac{1}{2}P_{1i} + \frac{1}{2}P_{2i}$$

Final P = average of initial Ps

$$= \boxed{\frac{5}{2} \text{ atm}}$$

b. Using (9.57):

$$\Delta G = nRT(X_1 \ln X_1 + X_2 \ln X_2)$$

$n = n_1 + n_2$, ~~X~~ X_1 = molar fraction of neon

X_2 = molar fraction of argon

Since the left compartment has 4 times the pressure of the right compartment and they have the same volume, there must be 4 times as much neon as argon, e.g.

$$n_1 = 4n_2 \qquad n_2 = 0.25 n_1$$

$$\Delta G = (n_1 + n_2) \cdot RT\left[\frac{n_1}{n_1+n_2} \ln\left(\frac{n_1}{n_1+n_2}\right) + \frac{n_2}{n_1+n_2} \ln\left(\frac{n_2}{n_1+n_2}\right)\right]$$

$$\Delta G = 1.25 n_1 \cdot RT\left(\frac{n_1}{1.25n_1}\ln\left(\frac{n_1}{1.25n_1}\right) + \frac{0.25n_1}{1.25n_1}\ln\left(\frac{0.25n_1}{1.25n_1}\right)\right)$$

$$= 1.25\cdot 1000\,\text{mol}\cdot 8.315\,\text{J/mol}\cdot\text{K}\cdot 300\,\text{K}\cdot\left(\frac{1}{5}\ln\left(\frac{1}{5}\right) + \frac{4}{5}\ln\left(\frac{4}{5}\right)\right)$$

$$= \boxed{-1.56\cdot 10^6\,\text{J}}$$

c. $\Delta S = -nR(x_1 \ln x_1 + x_2 \ln x_2)$

$$= -1.25\cdot 1000\cdot 8.315\cdot\left(\frac{1}{5}\ln\frac{1}{5} + \frac{4}{5}\ln\frac{4}{5}\right)$$

$$\boxed{\Delta S = 5.2\cdot 10^3\,\text{J/K}}$$

10.2 For an ideal gas: $pV=nRT$

$$\beta=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p=\frac{1}{V}\cdot\frac{nR}{p}=\frac{1}{T}\longrightarrow\infty$$

as $T\to 0$.

This violates (10.25)

For a VdW gas:

$\left(p+\frac{a}{v^2}\right)(v-b)=RT$. Note that β can be written in terms of the specific volume or the extensive, actual volume (v or V). In Part A we used the extensive volume. Here we use the specific volume: $\beta=\frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p$

$$p=\frac{RT}{v-b}-\frac{a}{v^2}$$

Cyclic Relation: $\left(\frac{\partial v}{\partial T}\right)_p=\dfrac{-\left(\frac{\partial p}{\partial T}\right)_v}{\left(\frac{\partial p}{\partial v}\right)_T}$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{v-b}$$

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

$$\beta = \frac{1}{V} \cdot \frac{-\frac{R}{v-b}}{\frac{-RT}{(V-b)^2} + \frac{2a}{V^3}} = \frac{R(v-b)}{vRT - \frac{2a(v-b)^2}{v^2}}$$

If we assume that $\lim_{T \to 0} V$ is nonzero (which is true; lowering a substance to absolute zero does not make it disappear), then

$$\lim_{T \to 0} \beta = \frac{R(v-b)}{-\frac{2a(v-b)^2}{v^2}} \neq 0,$$ which

again violates (10.25).

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We could solve this equation using the quadratic formula, but that's a bit cumbersome. Instead, recall from Problem 5.24 that without the quadratic term, the solution would be $P = 15.3$ kbar. Plugging in this value of P, we can estimate the size of the quadratic term as

$$\frac{1}{2}\kappa_T V_g P^2 \approx \frac{1}{2}(3\times10^{-3}\ \text{kbar}^{-1})(0.531\ \text{kJ/kbar})(15.3\ \text{kbar})^2 = 0.186\ \text{kJ}.$$

(I've expressed V_g in kJ/kbar, as discussed in Problem 5.25.) With this estimate of the correction term due to compression, we have for the transition pressure

$$P = \frac{1}{V_g - V_d}(2.9\ \text{kJ} + 0.186\ \text{kJ}) = \frac{3.086\ \text{kJ}}{.189\ \text{kJ/kbar}} = 16.3\ \text{kbar},$$

only about 7% higher than what we got neglecting compression. The small effect of the correction, moreover, justifies the various approximations made in this solution.

Problem 5.28. (Calcite and aragonite.)

(a) The table on page 404 gives the molar Gibbs free energies of formation of both calcite and aragonite, with the value for calcite being lower by 1.0 kJ. This means that the Gibbs free energy of a mole of calcite is less than that of a mole of aragonite by this amount, under standard conditions. Calcite is therefore the more stable phase, at room temperature and atmospheric pressure.

(b) In analogy with the diamond-graphite system, we can imagine plotting G vs. P (at fixed T) for both calcite and aragonite. The slopes of the two graphs are $V_c = 3.693$ kJ/kbar and $V_a = 3.415$ kJ/kbar, according to the data in the table and the conversion factor derived in Problem 5.25. Since the volume of aragonite is less, it should become stable at high pressure, that is, the two lines should intersect at some $P > 0$. For convenience, I'll set $G_c = 0$ at $P = 0$; then $G_a = 1.0$ kJ at $P = 0$. The equations of the two lines are then

$$G_c = V_c P \qquad \text{and} \qquad G_a = V_a P + (1.0\ \text{kJ}).$$

Equating these two expressions and solving for P gives the transition pressure,

$$P = \frac{1.0\ \text{kJ}}{\mathrm{V_c - V_a}} = \frac{1.0\ \text{kJ}}{0.278\ \text{kJ/kbar}} = 3.6\ \text{kbar}.$$

Problem 5.29. (The aluminosilicate system.)

(a) The $\Delta_f G$ values on page 404 indicate that at room temperature and atmospheric pressure, kyanite has the lowest Gibbs free energy of the three phases. Furthermore, it also has the lowest molar volume of the three; this means that increasing the pressure causes its G value to increase more slowly than those of the other two phases. Since it starts out lowest and increases slowest, it will never intersect the G values of the other phases (in contrast to the graphite-diamond case illustrated in Figure 5.15).

(b) For either phase, $(\partial G/\partial T)_P = -S$. Integrating this relation from T_1 to T_2 gives

$$G(T_2) - G(T_1) = -\int_{T_1}^{T_2} S(T)\,dT.$$

If we write this equation separately for two different phases and then subtract one equation from the other, the G's become ΔG's and the S becomes ΔS, so we obtain the desired result,

$$\Delta G(T_2) = \Delta G(T_1) - \int_{T_1}^{T_2} \Delta S(T)\,dT.$$

(c) Taking ΔS to be independent of T, we can pull it outside the integral to obtain

$$\Delta G(T_2) = \Delta G(T_1) - (T_2 - T_1)\cdot \Delta S.$$

If we take T_2 to be the temperature at which the phase transition occurs (the two phases are in equilibrium), then $\Delta G(T_2) = 0$. Solving for T_2 then gives simply

$$T_2 = T_1 + \frac{\Delta G(T_1)}{\Delta S}.$$

Our thermodynamic data is at 298 K, so we'll use this value for T_1. For the kyanite-andalusite transition, $\Delta G(T_1) = 1.22$ kJ (for one mole of material), while $\Delta S = 9.41$ J/K. Therefore, the temperature at which andalusite becomes more stable than kyanite should be approximately

$$T_2 = 298\text{ K} + \frac{1.22\text{ kJ}}{9.41\text{ J/K}} = 428\text{ K}.$$

Similarly, for the kyanite-sillimanite transition,

$$T_2 = 298\text{ K} + \frac{2.89\text{ kJ}}{12.30\text{ J/K}} = 533\text{ K}.$$

And for the andalusite-sillimanite transition,

$$T_2 = 298\text{ K} + \frac{1.67\text{ kJ}}{2.89\text{ J/K}} = 876\text{ K}.$$

So at atmospheric pressure, kyanite should be stable up to (approximately) 428 K, andalusite should be stable from 428 K up to 876 K, and sillimanite should be stable above 876 K.

(d) The change in entropy as the temperature is increased is given by equation 3.50,

$$S(T_2) = S(T_1) + \int_{T_1}^{T_2} \frac{C_P}{T}\,dT.$$

If we write this equation for two different phases and then subtract, we obtain

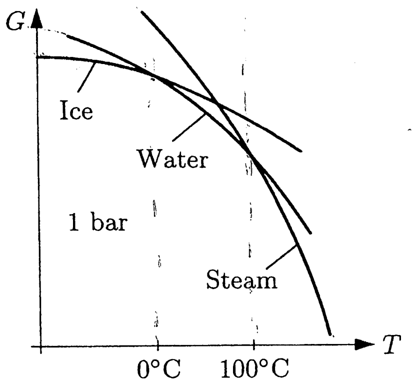
$$\Delta S(T_2) = \Delta S(T_1) + \int_{T_1}^{T_2} \frac{\Delta C_P}{T}\, dT.$$

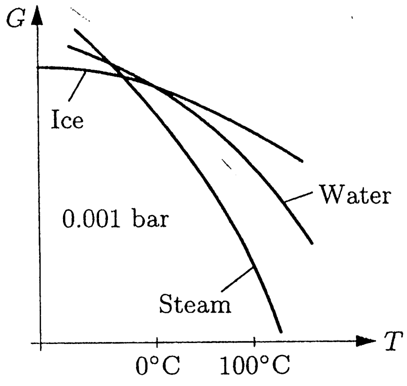
Suppose, for the sake of a rough estimate, that ΔC_P is independent of temperature. Then

$$\Delta S(T_2) = \Delta S(T_1) + \Delta C_P \cdot \ln(T_2/T_1).$$

For kyanite → andalusite, $\Delta C_P = 1.01$ J/K (at room temperature). Taking $T_1 = 298$ K and $T_2 = 428$ K, I find that the final term in this equation is 0.37 J/K, compared to $\Delta S(T_1) = 9.41$ J/K. So over this range, ΔS is reasonably independent of temperature. However, for andalusite → sillimanite, $\Delta C_P = 1.80$ J/K and we should take $T_2 = 876$ K; with these numbers I get a correction term of 1.94 J/K, compared to $\Delta S(T_1) = 2.89$ J/K. With ΔS varying by nearly 70% over the temperature range of interest, I conclude that the calculated temperature of the transition could be off by as much as 100–200 K. To make a significantly improved calculation, however, we would really need heat capacity data over the whole temperature range.

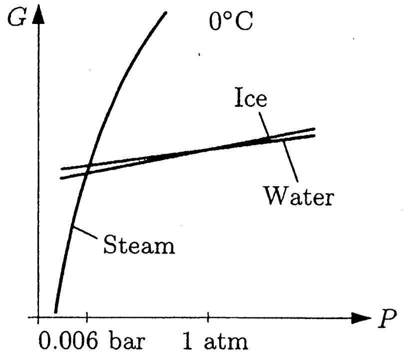
Problem 5.30. The slope of a graph of G vs. T is $-S$, so the slope of each graph should be negative, and become more negative with increasing temperature. Furthermore, at any given temperature, the stable phase should have the lowest value of G. For H_2O at atmospheric pressure, the stable phase is ice below 0°C, water between 0°C and 100°C, and steam above 100°C. The plot at left below shows these features qualitatively.

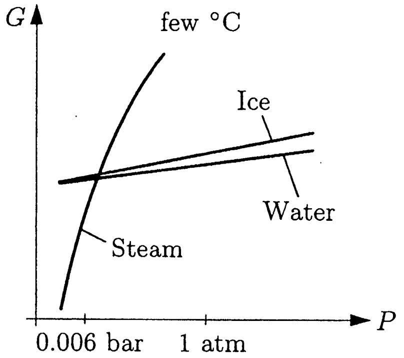




As the pressure is reduced, the relation $(\partial G/\partial P)_T = V$ tells us that the Gibbs free energy of each phase will decrease. However, that of the gas phase will decrease the fastest by far, since its volume is so much greater. At pressures below the triple point (0.006 bar), there is no temperature at which liquid water is stable. So at 0.001 bar, the graphs of G vs. T would look something like the plot above right.

Problem 5.31. The slope of a graph of G vs. P is V, so the slope of each graph should be positive, with the ice graph slightly steeper than the water graph and the steam graph much steeper than either. The steam graph, furthermore, should have a significant downward curvature due to its compressibility. At any given temperature, the curve for the stable phase should be the lowest of the three. At 0°C, the stable phase is steam up to 0.006 bar, ice from there up to 1 bar, and water above 1 bar. The graph at left below shows these features qualitatively.





As the temperature is raised, the relation $(\partial G/\partial T) = -S$ tells us that the Gibbs free energy of each phase will decrease. That of the gas phase will decrease the most, since it has the most entropy, while that of the solid will decrease the least. Above 0.01°C, the intersection of the solid and liquid G curves moves to the left of the gas curve, indicating that the solid is no longer stable at any temperature. At a few degrees Celsius, the graphs would look something like the plot above right.

Problem 5.32. (The water-ice phase boundary.)

(a) As ice melts into water the change in entropy (or the latent heat) is positive, while the change in volume is negative (since ice is less dense), so the slope of the phase boundary, $\Delta S/\Delta V$, must be negative. In more fundamental terms, converting ice to water lets the entropy of the environment increase (by making more volume available), and this effect is more important at high pressure since $P = T(\partial S/\partial V)$. So high pressures tend to push the equilibrium in the direction of the phase that takes up less volume.

(b) Instead of considering a mole of ice/water, let's just consider one gram. Then the latent heat is 333 J, the volume of the ice is $(917{,}000)^{-1}\ \text{m}^3 = 1.091 \times 10^{-6}\ \text{m}^3$, and the volume of the water is $1.000 \times 10^{-6}\ \text{m}^3$. Therefore the slope of the phase boundary is

$$\frac{dP}{dT} = \frac{L}{T\,\Delta V} = \frac{333\ \text{J}}{(273\ \text{K})(-.091 \times 10^{-6}\ \text{m}^3)} = -1.35 \times 10^7\ \text{Pa/K} = -135\ \text{bar/K}.$$

So if the temperature decreases by one degree (from 0 to −1°C), the pressure must increase by 135 bars to remain on the phase boundary. In other words, ice will melt at −1°C if the pressure is above 135 bars (or 133 atmospheres).

(c) Treating the glacier ice as a fluid, the increase in pressure at depth z is simply $\rho g z$, where ρ is the density. (To derive this formula, consider a column of ice extending down to depth z. The weight of the column per unit area is $\rho g z$, and this must be balanced by the pressure from below.) In our case, to reach a pressure of 135 bars,

$$z = \frac{P}{\rho g} = \frac{135 \times 10^5\ \text{N/m}^2}{(917\ \text{kg/m}^3)(9.8\ \text{N/kg})} = 1500\ \text{m}.$$

That's pretty deep, just to lower the melting temperature by one degree. Apparently the flow of glaciers is not caused primarily by lowering of the melting point under pressure.

(d) The blade of an ice skate measures a few millimeters across by perhaps 25 cm long, so the total area is perhaps 10 cm^2. Even if you're leaning on the "corner" of the blade, the total area in contact with the ice is probably more than 1 $\text{cm}^2 = 10^{-4}\ \text{m}^2$. If your mass is 50 kg, then your weight is about 500 N so the pressure on the blade is roughly $(500\ \text{N})/(10^{-4}\ \text{m}^2) = 5 \times 10^6\ \text{Pa} = 50$ bars. Under this pressure the melting temperature drops by only $50/135 \approx .4°\text{C}$. This mechanism of friction reduction would work *only* if the ice temperature is already within less than half a degree of melting, and even then, only when you're minimizing the area of the blade in contact with the ice. In practice, the ability to glide doesn't depend so critically on the ice temperature or on how the blade touches the ice, so I don't think this mechanism can be very important.

Problem 5.33. The flaw in the inventor's reasoning is that the weight that can be lifted by the water as it freezes into ice is limited, because too much weight would apply enough pressure to lower the freezing point of the water below −1°C, and then the water wouldn't freeze at all. Let the water in the cylinder have height h_w and cross-sectional area A. When it freezes into ice, its height increases to h_i. If the mass it lifts is m, then the work performed upon freezing is $mg(h_i - h_w)$. If L is the heat needed to remelt the ice, then the efficiency of the engine is

$$e = \frac{W}{Q_h} = \frac{mg(h_i - h_w)}{L}.$$

If the pressure on the system with the weight absent is atmospheric pressure, then there's really no need for the high-temperature reservoir to be hotter than $T_h = 0°\text{C}$; higher T_h would just lead to wasted heat as the system is cooled back to 0°C. If T_c is the temperature of the cold reservoir, then according to the Clausius-Clapeyron relation, the maximum pressure we can add to the system without shifting the freezing point below T_c is

$$dP = \frac{L}{T_h(V_i - V_w)}(T_h - T_c),$$

where $V_i = h_i A$ and $V_w = h_w A$ are the volumes of the two phases, and I've used T_h in the denominator because L refers to the heat input from the hot reservoir. Setting this quantity equal to the pressure exerted by the lifted mass gives

$$\frac{mg}{A} = \frac{L(T_h - T_c)}{T_h A(h_i - h_w)}, \qquad \text{or} \qquad \frac{mg(h_i - h_w)}{L} = \frac{T_h - T_c}{T_h}.$$

In other words, the maximum efficiency of the engine is $1 - (T_c/T_h)$.

Problem 5.34. (Liquid-solid phase boundary of ^{3}He.)

(a) The denser phase is always the one that is stable at higher pressure, according to $(\partial G/\partial P)_T = V$: Smaller volume implies a shallower slope to the G vs. P curve and hence a lower value of G than the other phase at sufficiently high pressures. In our case,

Problem 5.40. For the reaction albite → jadeite + quartz, the standard ΔG value, at room temperature and atmospheric pressure, is

$$\Delta G = -2852.1\text{ kJ} - 856.6\text{ kJ} + 3711.5\text{ kJ} = 2.8\text{ kJ},$$

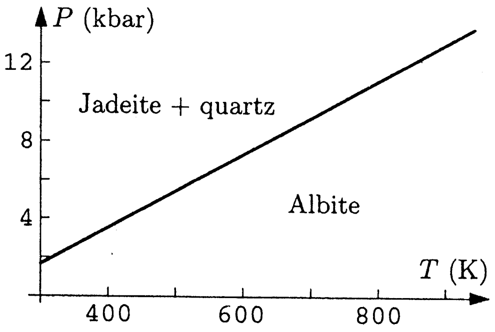
according to the data on page 405. Because this number is positive, albite is more stable than jadeite + quartz under these conditions. However, the jadeite-quartz combination takes up considerably less volume than albite, so it should become stable at high pressure. Solving for the transition pressure as in Problems 5.24 and 5.28, we obtain

$$P = \frac{2.8\text{ kJ}}{\Delta \mathrm{V}} = \frac{2.8\text{ kJ}}{10.007\text{ kJ/kbar} - 6.040\text{ kJ/kbar} - 2.269\text{ kJ/kbar}} = 1.65\text{ kbar}.$$

The slope of the phase boundary, meanwhile, is given by the Clausius-Clapeyron relation:

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{207.4\text{ J/K} - 133.5\text{ J/K} - 41.8\text{ J/K}}{1.70\text{ J/bar}} = 18.9\text{ bar/K}.$$

The diagram at right shows the regions of stability of the two phases, assuming that ΔS and ΔV are independent of temperature and pressure, hence that the phase boundary is a straight line. As $T \to 0$, however, the slope of the phase boundary would have to be horizontal, as in Figure 5.17, according to the third law of thermodynamics.



Problem 5.41. (Effect of total pressure on vapor pressure.)

(a) We want to consider the change in the chemical potentials of the two phases under an infinitesimal change in total pressure. For the gas, according to equation 5.40,

$$\mu_g = \text{constant} + kT \ln P_v,$$

where P_v is the partial pressure of the gas, assumed to be equal to the vapor pressure. Differentiating with respect to the total pressure P, we obtain

$$\frac{d\mu_g}{dP} = \frac{kT}{P_v}\frac{dP_v}{dP}.$$

(I'll write the derivatives as total derivatives, even though they're really partial derivatives, with temperature understood to be held fixed.) Meanwhile, for the liquid, $\mu = G/N$ (since it remains pure), so

$$\frac{d\mu_l}{dP} = \frac{1}{N_l}\frac{dG}{dP} = \frac{V_l}{N_l}.$$

For the two phases to remain in equilibrium as we change the total pressure, the changes in their chemical potentials must be equal, so

$$\frac{kT}{P_v}\frac{dP_v}{dP} = \frac{V_l}{N_l} \qquad \text{or} \qquad \frac{dP_v}{dP} = \frac{V_l}{N_l kT} P_v.$$

This is the desired differential equation for the function $P_v(P)$.

(b) The solution to this equation is a simple exponential function,

$$P_v(P) = (\text{constant}) \cdot e^{PV/NkT},$$

where I've dropped the l subscripts on the V and N in the exponent. Plugging in $P = P_v$ (for the initial situation with no inert gas), this equation becomes

$$P_v(P_v) = (\text{constant}) \cdot e^{P_v V/NkT}.$$

Dividing the previous equation by this one cancels out the constant, leaving us with

$$\frac{P_v(P)}{P_v(P_v)} = e^{(P-P_v)V/NkT},$$

where again the quantity V/N in the exponent is for the liquid.

(c) For water at 25°C, the vapor pressure is only 0.03 bar, so the P_v in the exponent is negligible compared to $P = 1$ bar. It's simplest to take N to be one mole, so $Nk = R$ and $V = 18\ \text{cm}^3$; the exponential factor is thus

$$\exp\left(\frac{(10^5\ \text{N/m}^2)(18 \times 10^{-6}\ \text{m}^3)}{(8.31\ \text{J/K})(298\ \text{K})}\right) = \exp(0.00073) = 1.00073,$$

implying that the vapor pressure is greater by 0.07% than its value in the absence of the air. More generally, the quantity PV/NkT, where V/N refers to the *liquid*, will always be much less than 1 as long as the molar volume of the liquid is much less than that of the gas (for which $PV/NkT \approx 1$). Only near the critical point (which is at fairly high pressures for most fluids) would this ratio be comparable to 1.

Problem 5.42. (Relative humidity and dew point.)

(a) The result of Problem 5.35 for the shape of the vapor pressure curve was

$$P = P_0 e^{-L/RT}.$$

Using the data for $T = 25$°C from Figure 5.11, we have

$$\frac{L}{R} = \frac{43{,}990\ \text{J/mol}}{8.315\ \text{J/mol·K}} = 5290\ \text{K};$$

solving for the constant P_0 therefore gives

$$P_0 = (0.0317\ \text{bar}) \exp\Big(5290\ \text{K}/298\ \text{K}\Big) = 1.626 \times 10^6\ \text{bar}.$$

I then plotted the vapor pressure curve using the *Mathematica* instruction

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Plot[1626000*Exp[-5290/(t+273)],{t,0,40},Frame->True]
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which produced the graph on the following page.

Problem 5.74. According to equations 5.69 and 5.70,

$$\begin{aligned} N_A\mu_A + N_B\mu_B &= N_A\Big(\mu_0 - \frac{N_BkT}{N_A}\Big) + N_B\Big(f + kT\ln\frac{N_B}{N_A}\Big) \\ &= N_A\mu_0 - N_BkT + N_Bf + N_BkT\ln(N_B/N_A), \end{aligned}$$

which is the same as expression 5.68 for G. Therefore, $G = N_A\mu_A + N_B\mu_B$.

Problem 5.75. Expression 5.61 (for an ideal mixture) should apply to a dilute solution when the ideal mixture is also dilute—that is, when $N_B \ll N_A$. Expression 5.68 (for a dilute solution) should apply to an ideal mixture when the solution is ideal—that is, when the B molecules "behave" just like A molecules, in terms of their sizes and interactions. To show the agreement between the two expressions under these circumstances, I'll start with equation 5.61. Recall first that $x = N_B/N_{\text{total}}$, $1-x = N_A/N_{\text{total}}$, so $(1-x)G_A^\circ = N_AG_A^\circ/N_{\text{total}} = N_A\mu_A^\circ$, and similarly, $xG_B^\circ = N_B\mu_B^\circ$. In the last term, since N_{total} is assumed to be Avogadro's number, we can write $R = N_{\text{total}} \cdot k$. Equation 5.61 is therefore equivalent to

$$\begin{aligned} G &= N_A\mu_A^\circ + N_B\mu_B^\circ + kT\Big[N_B\ln\frac{N_B}{N_A+N_B} + N_A\ln\frac{N_A}{N_A+N_B}\Big] \\ &= N_A\mu_A^\circ + N_B\mu_B^\circ - kT\Big[N_B\ln\Big(\frac{N_A}{N_B}+1\Big) + N_A\ln\Big(1+\frac{N_B}{N_A}\Big)\Big]. \end{aligned}$$

Now assume that this ideal mixture is also dilute, so $N_B \ll N_A$. Then the 1 in the first logarithm can be dropped, while the second logarithm can be approximated as simply N_B/N_A. With these approximations,

$$G \approx N_A\mu_A^\circ + N_B\mu_B^\circ - kT\big[N_B\ln(N_A/N_B) + N_B\big],$$

up to correction terms that are small compared to the terms that are shown. But this expression is the same as equation 5.68, if we identify

$$f(T,P) = \mu_B^\circ(T,P) \qquad \text{(ideal, dilute solution)}.$$

In other words, the mysterious function $f(T,P)$, in the case of a dilute solution that is also ideal, is just the chemical potential of a system of pure B molecules at the same temperature and pressure.

Problem 5.76. (Osmotic pressure of seawater.)

(a) Let's take as our system a kilogram of seawater at room temperature. Then the volume is approximately one liter (10^{-3} m^3). The total mass of solute is 35 g, and the average atomic mass of sodium and chlorine is about 29.2 g/mol, so the number of moles of solute is

$$n_B = \frac{35\text{ g}}{29.2\text{ g/mol}} = 1.12\text{ mol}.$$

Therefore, by van't Hoff's formula, the osmotic pressure is

$$P_2 - P_1 = \frac{n_B RT}{V} = \frac{(1.12\text{ mol})(8.315\text{ J/mol·K})(300\text{ K})}{10^{-3}\text{ m}^3} = 3.0 \times 10^6\text{ Pa} \approx 30\text{ atm}.$$

(b) If you apply an excess pressure just barely greater than the osmotic pressure to the seawater, and force 1 liter of it through an osmotic membrane, the work performed is

$$P\,\Delta V = (3.0 \times 10^6\text{ Pa})(10^{-3}\text{ m}^3) = 3000\text{ J}.$$

This isn't much work—less than 1/1000 of a kilowatt-hour. As usual, though, this number represents the absolute minimum, and in practice the work required will be greater. First, to get the water to go through the membrane at an acceptable rate, you'll need to apply more than the minimum pressure. Second, the membrane probably won't be perfect, so some salt will get through and you'll need to repeat the process several times to reduce the salinity to an acceptable level.

Problem 5.77. When the difference in fluid level between the two sides of the container is Δh, the difference in pressure should be $\rho g\,\Delta h$, where ρ is the density of the solution (close enough to the density of pure water). Plugging this in for the pressure difference in van't Hoff's formula gives

$$\rho g\,\Delta h = \frac{n_B RT}{V}.$$

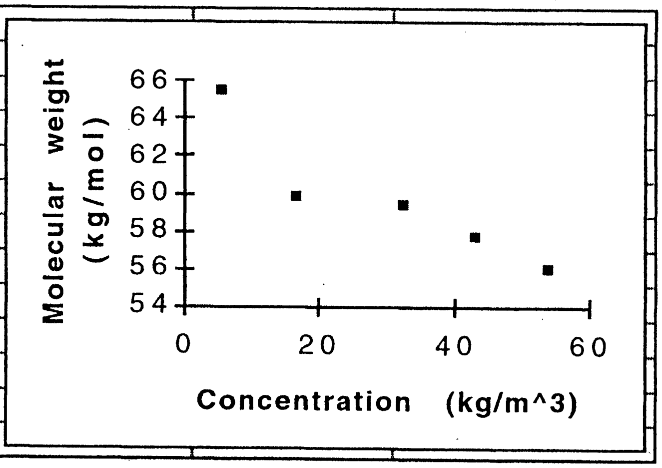
But the number of moles of solute, n_B, is equal to mass of the solute, m, divided by its molecular weight, M, in grams per mole. Therefore,

$$\rho g\,\Delta h = \frac{mRT}{MV}, \qquad \text{or} \qquad M = \frac{RT}{\rho g} \cdot \frac{m/V}{\Delta h}.$$

I used this equation to calculate M for each of the five data points given (see the spreadsheet below). The coefficient $RT/\rho g$ is

$$\frac{RT}{\rho g} = \frac{(8.315\text{ J/mol·K})(276\text{ K})}{(1000\text{ kg/m}^3)(9.8\text{ N/kg})} = 0.234\text{ m}^4/\text{mol}.$$

Conc. (kg/^3)	Delta-h (m)	M (kg/mol)
5.6	0.02	65.52
16.6	0.065	59.76
32.5	0.128	59.4141
43.4	0.176	57.7023
54	0.226	55.9115



From the graph you can see that the calculated value of M does depend somewhat on the concentration, in violation of van't Hoff's formula. However, the trend indicates a value of $M \approx 66{,}000$ g/mol in the limit of low concentration where the formula should be valid.

Problem 5.81. For a solution of solute B in solvent A, in equilibrium with a solid of pure A, the chemical potentials of A must be equal for the two phases:

$$\mu_{A,\text{liq}} = \mu_{A,\text{solid}}.$$

Using equation 5.69 to rewrite the left-hand side, this condition becomes

$$\mu_{(}T,P) - \frac{N_B kT}{N_A} = \mu_{\text{solid}}(T,P).$$

Now let T_0 be the temperature at which the pure liquid would be in equilibrium with the solid (at fixed pressure P). Expanding each chemical potential about T_0, we have

$$\mu_0(T_0,P) + (T-T_0)\frac{\partial \mu_0}{\partial T} - \frac{N_B kT}{N_A} = \mu_{\text{solid}}(T_0,P) + (T-T_0)\frac{\partial \mu_{\text{solid}}}{\partial T}.$$

The first term on each side of this equation cancels by the assumption that T_0 is the temperature at which the pure liquid is in equilibrium with the solid. Each $\partial\mu/\partial T$ is minus the entropy per particle for that phase, so

$$-(T-T_0)\left(\frac{S}{N}\right)_{\text{liq}} - \frac{N_B kT}{N_A} = -(T-T_0)\left(\frac{S}{N}\right)_{\text{solid}}.$$

Now set the N under each S equal to N_A, the number of molecules of solvent; the S's then apply to the same quantity, and our relation becomes

$$(T-T_0)(S_{\text{liq}} - S_{\text{solid}}) = -N_B kT, \qquad \text{or} \qquad T - T_0 = -\frac{N_B kT^2}{L},$$

where in the last step I've used $L = \Delta S/T_0 \approx \Delta S/T$, taking L to represent the latent heat for transformation of N_A molecules of solid into liquid. The minus sign in this result indicates that adding a solute *lowers* the freezing point of a liquid. This makes sense because mixing is allowed in the liquid phase but not the solid phase, so we would expect the entropy of mixing to increase the stability of the liquid relative to that of the solid. We saw the same result qualitatively in the last part of Section 5.4.

Problem 5.82. To compute the freezing point of seawater, we need to know that a kilogram of seawater contains 1.2 moles of salt ions, as computed at the bottom of page 207. We also need the latent heat of the ice-water transformation, which from page 33 is 333 J/g or 333,000 J/kg. Plugging these numbers into the formula derived in the previous problem gives

$$\Delta T = -\frac{n_B RT^2}{L} = -\frac{(1.2\text{ mol})(8.31\text{ J/mol}\cdot\text{K})(273\text{ K})^2}{333{,}000\text{ J/kg}} = -2.2\text{ K}.$$

The freezing point of seawater should therefore be −2.2°C.

Problem 5.83. For each reaction shown, the equilibrium condition is the same as the reaction equation, with the name of the species replaced by its chemical potential and ↔ replaced by =:

(a) $2\mu_{\text{H}} = \mu_{\text{H}_2}$

(b) $2\mu_{\text{CO}} + \mu_{\text{O}_2} = 2\mu_{\text{CO}_2}$

(c) $\mu_{\text{methane}} + 2\mu_{\text{O}_2} = 2\mu_{\text{water}} + 2\mu_{\text{CO}_2}$

(d) $\mu_{\text{H}_2\text{SO}_4} = 2\mu_{\text{H}^+} + \mu_{\text{SO}_4^{2-}}$

(e) $2\mu_p + 2\mu_n = \mu_{\text{He}}$

Problem 5.84. I'll use the convention that all pressures are expressed in atmospheres, so $P^\circ = 1$ and the total pressure is 400:

$$P_{\text{N}_2} + P_{\text{H}_2} + P_{\text{NH}_3} = 400.$$

The initial mixture consists of three parts hydrogen to one part nitrogen, and this proportion is preserved as the reaction takes place, so $P_{\text{H}_2} = 3P_{\text{N}_2}$ and hence

$$4P_{\text{N}_2} + P_{\text{NH}_3} = 400. \tag{1}$$

Meanwhile, the law of mass action tells us that

$$\frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3} = K.$$

But again, $P_{\text{H}_2} = 3P_{\text{N}_2}$, so

$$\frac{P_{\text{NH}_3}^2}{27P_{\text{N}_2}^4} = K \qquad \text{or} \qquad P_{\text{NN}_3} = P_{\text{N}_2}^2 \cdot \sqrt{27K} = P_{\text{N}_2}^2 \cdot 0.0432,$$

where I've plugged in the value $K = 6.9 \times 10^{-5}$. Plugging this relation into equation 1 then gives the quadratic equation

$$(0.0432)P_{\text{N}_2}^2 + 4P_{\text{N}_2} - 400 = 0,$$

whose solutions are

$$P_{\text{N}_2} = \frac{-4 \pm \sqrt{16 + 4(0.0432)(400)}}{2(0.0432)} = -46.3 \pm \overset{106.78}{\cancel{96.2}} = \overset{60.48}{\underset{-153.08}{\cancel{-142.5 \text{ or } 49.9.}}}$$

60.48

The negative solution is obviously unphysical, so the partial pressure of N_2 at equilibrium
must be roughly ~~50~~ atm. That means the partial pressure of H_2 must be three times
181.4 as much, or ~~150~~ atm, and the partial pressure of ammonia must make up the remaining
158 ~~200~~ atm to give 400 atm total. The ratio of nitrogen atoms in ammonia to nitrogen atoms
in N_2 is then ~~200/(2·50) = 2/1~~, meaning that ~~2/3~~ of all the nitrogen atoms are in ammonia.

$$\frac{158}{2 \cdot 60.48} = \frac{1.3}{1} \qquad \frac{1.3}{1.3+1}$$

Additional problem HW#8

a) $\gamma = \frac{\partial U}{\partial L}\Big|_{S,N}$

b) Since $U(S, L, N)$ is homogeneous of order 1 we know that:

$$U = \frac{\partial U}{\partial S}\Big|_{L,N} S + \frac{\partial U}{\partial L}\Big|_{S,N} L + \frac{\partial U}{\partial N}\Big|_{S,L} N$$

$$U = TS + \gamma L + \mu N$$

this expression implies

ⓐ $dU = TdS + SdT + \gamma dL + Ld\gamma + \mu dN + Nd\mu$

but we know from the problem that

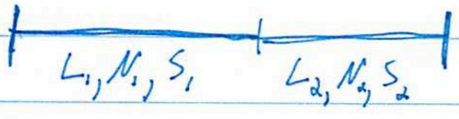
ⓑ $dU = TdS + \gamma dL + \mu dN$

Compare ⓐ and ⓑ to find

$$\boxed{SdT + Ld\gamma + Nd\mu = 0}$$ similar to Gibbs-Duhem

c) Following similar arguments to in class:

Consider a composite system of two joined rubber bands held at constant $L_{TOT} = L_1 + L_2$



$S_{TOT} = S_1 + S_2$

$N_{TOT} = N_1 + N_2$

The energy minimum principle tells us the system will equilibrate such that perturbations away from equilibrium correspond to $\Delta U \geq 0$.

Only allow entropy exchange at constant total entropy (i.e. $dS_1 = -dS_2$ -or- $\Delta S_1 = -\Delta S_2$)

$$\Delta U = \Delta U_1 + \Delta U_2$$

$$= + \left.\frac{\partial U_1}{\partial S_1}\right|_{L_1,N_1} \Delta S_1 + \frac{1}{2} \left.\frac{\partial^2 U_1}{\partial S_1^2}\right|_{L_1,N_1} (\Delta S_1)^2 + \cdots$$

$$+ \left.\frac{\partial U_2}{\partial S_2}\right|_{L_2,N_2} \Delta S_2 + \frac{1}{2} \left.\frac{\partial^2 U_2}{\partial S_2^2}\right|_{L_2,N_2} (\Delta S_2)^2 + \cdots$$

$\downarrow$ since $\frac{\partial U_1}{\partial S_1} = \frac{\partial U_2}{\partial S_2} = T$ at eq.

$$\Delta U = U^{eq} + \frac{1}{2}\left(\left.\frac{\partial T}{\partial S_1}\right|_{L_1,N_1} + \left.\frac{\partial T}{\partial S_2}\right|_{L_2,N_2} \right) (\Delta S_1)^2 + \cdots$$

Since $\Delta U \geq 0$ this implies that

$\left.\frac{\partial T}{\partial S}\right|_{L,N}$ must be positive in both parts.

i.e. $\boxed{\left.\frac{\partial S}{\partial T}\right|_{L,N} \geq 0 \text{ for a rubber band in stable equilibrium}}$

(It is *not* possible for it to be negative in one part, since that part could be made smaller, eventually leading to $\Delta U < 0$ as in arguments in class.)

d) Let $\boxed{A = U - TS}$

then $dA = -S\,dT + \gamma\, dL + \mu\, dN$

and $A(T, L, N)$

e) from above, a maxwell relation implies

$$\boxed{\left.\frac{\partial \gamma}{\partial T}\right|_{L,N} = -\left.\frac{\partial S}{\partial L}\right|_{T,N}} = \left.\frac{\partial^2 A}{\partial L\, \partial T}\right|_{N}$$

f) $\left.\frac{\partial \gamma}{\partial T}\right|_{L,N} > 0$ so, $\left.\frac{\partial S}{\partial L}\right|_{T,N} < 0$

Cyclic rule: $\left.\frac{\partial T}{\partial L}\right|_{S,N} \left.\frac{\partial L}{\partial S}\right|_{T,N} \left.\frac{\partial S}{\partial T}\right|_{L,N} = -1$

$$\left.\frac{\partial T}{\partial L}\right|_{S,N} = -\underbrace{\left.\frac{\partial S}{\partial L}\right|_{T,N}}_{\substack{<0 \\ \text{part e,f}}} \underbrace{\left.\frac{\partial T}{\partial S}\right|_{L,N}}_{>0 \text{ part c}}$$

$$\Rightarrow \boxed{\left.\frac{\partial T}{\partial L}\right|_{S,N} > 0}$$

g) The rubber band gets hotter when stretched, in agreement with part f.