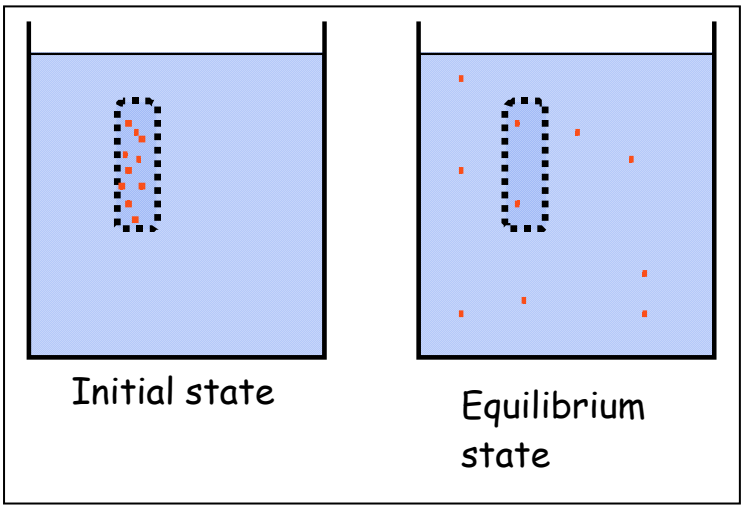
BE.011/2.772
Problem Set 3
Due March 3, 2004

1. Dialysis is common laboratory procedure used to remove low molecular weight solutes from protein solutions. Example situations include: removal of removal of free, unreacted label after fluorescently labeling a protein; and removal of urea from a denatured protein solution to allow refolding of the protein. The protein solution is sealed inside a dialysis bag or tubing and placed in container with a large excess of pure water, as shown in the figure. The system is then allowed to come to equilibrium. For this problem, consider an idealized system where the only solute in the dialysis bag is the low molecular weight solute (i.e., no protein is actually present.)



(a) Explain why the combined system of the protein solution (system "A") and the water (system "B") may be considered to be an isolated system.

The combined system can be considered an isolated system because neither the total matter, energy or volume changes. System A or B individually are open systems.

(b) Use a lattice model, with each individual water molecule occupying a single site in the lattice, to show that the entropy of System B is zero at the start of the experiment. Designate the number of water molecules N_{WB} and the number of total lattice sites M_B.

$$W = \binom{M_B}{N_{wB}} = \frac{M_B!}{(M_B - N_{wB})!N_{wB}!}$$

Since this is a liquid, we can assume that a molecule must occupy every site, so $M_B=N_{wB}$, we get

$$W = \frac{M_B!}{(M_B - M_B)!M_B!} = 1$$

$$S = k \ln W = 0$$

(c) Use a lattice model to express the entropy of system A at the start of the experiment in terms of the number of water molecules in system A, N_{wA}, the number of solute particles, N_s, and the total

number of lattice sites in system A, M_A. For your final expression, use an appropriate approximation to eliminate factorial expressions. You may assume that the water molecules and solute molecules are comparable in size.

Again assume that a molecule must occupy every site, so $M_A=N_s+N_{wA}$, we get

$$W = \frac{M_A!}{N_s!N_{wA}!}$$

Using Stirling's approximation,

$$W = \frac{\left(M_A/e\right)^{M_A}}{\left(N_S/e\right)^{N_S}\left(N_{wA}/e\right)^{N_{wA}}} = \frac{\left(M_A\right)^{M_A}}{\left(N_S\right)^{N_S}\left(N_{wA}\right)^{N_{wA}}}$$

$$S = k\ln W = k\ln\left[\frac{\left(M_A\right)^{M_A}}{\left(N_S\right)^{N_S}\left(N_{wA}\right)^{N_{wA}}}\right]$$

But $M_A=N_S+N_{wA}$, so

$$S = k\ln W = k\ln\left[\frac{\left(M_A\right)^{M_A}}{\left(M_A-N_{wA}\right)^{M_A-N_{wA}}\left(N_{wA}\right)^{N_{wA}}}\right]$$

(d) Now write an expression for the entropy of the combined system under the conditions where water and solute can freely pass through the dialysis membrane. For every solute molecule that crosses over to system B, a water molecule must cross over to system A. (You may want to keep track of the number of solute molecules by noting that $N_S=N_{SA}+N_{SB}$ and the number of water molecules by noting that $N_{WA}+N_{WB}=N_W$).

$$S = k\ln W_A W_B = k\ln\left[\frac{M_A!}{\left(M_A-N_{SA}\right)!N_{SA}!}\frac{M_B!}{\left(M_B-N_{SB}\right)!N_{SB}!}\right]$$

(e) Show that you can write the entropy expression in terms of one system variable (i.e., one parameter that changes value during the progress of the experiment), and briefly describe how to determine the equilibrium condition in terms of that variable and constants in the system. [You do not need to work out the equilibrium condition (lots of algebra involved) but feel free to predict what it is if you like.]

Write entropy in terms of N_{SA}.

$$N_S = N_{SA} + N_{SB}$$

$$S = k\ln\left[\frac{M_A!}{\left(M_A-N_{SA}\right)!N_{SA}!}\frac{M_B!}{\left(M_B-N_S+N_{SA}\right)!\left(N_S-N_{SA}\right)!}\right]$$

In order to determine the equilibrium point, use Stirling's approximation to simplify the expression, and then take the derivative.

$$S = k\ln\left[\frac{M_A^{\,M_A}}{(M_A - N_{SA})^{M_A - N_{SA}}\, N_{SA}^{\,N_{SA}}}\frac{M_B^{\,M_B}}{(M_B - N_S + N_{SA})^{M_B - N_S + N_{SA}}(N_S - N_{SA})^{N_S - N_{SA}}}\right]$$

$$\frac{S}{k} = M_A \ln M_A - (M_A - N_{SA})\ln(M_A - N_{SA}) - N_{SA}\ln N_{SA} + M_B \ln M_B$$
$$-(M_B - N_S + N_{SA})\ln(M_B - N_S + N_{SA}) - (N_S - N_{SA})\ln(N_S - N_{SA})$$

$$\frac{1}{k}\frac{dS}{dN_{SA}} = 0 + \ln(M_A - N_{SA}) + 1 - \ln N_{SA} - 1 + 0 - \ln(M_B - N_S + N_{SA}) - 1 + \ln(N_S - N_{SA}) + 1$$
$$= \ln\left[\frac{(M_A - N_{SA})(N_S - N_{SA})}{N_{SA}(M_B - N_S + N_{SA})}\right]$$

Set derivative equal to zero.

$$0 = \ln\left[\frac{(M_A - N_{SA})(N_S - N_{SA})}{N_{SA}(M_B - N_S + N_{SA})}\right]$$
$$\Rightarrow (M_A - N_{SA})(N_S - N_{SA}) = N_{SA}(M_B - N_S + N_{SA})$$

Dividing both sides by $M_A M_B$, and substituting in $N_{SB}=N_S+N_{SA}$

$$\frac{(M_A - N_{SA})(N_{SB})}{M_A M_B} = \frac{N_{SA}(M_B - N_{SB})}{M_A M_B}$$
$$\left(1 - \frac{N_{SA}}{M_A}\right)\frac{N_{SB}}{M_B} = \frac{N_{SA}}{M_A}\left(1 - \frac{N_{SB}}{M_B}\right)$$
$$\frac{N_{SA}}{M_A} = \frac{N_{SB}}{M_B}$$

When this is the case, the concentrations are equal.

(f) Is work done in the approach to equilibrium? Explain why or why not.

Work is not done in the approach to equilibrium, because there is no volume change associated with either system.

$$\delta w = pdV = 0.$$

(g) Does the internal energy U of the system change? Explain why or why not.

Since we are assuming an isolated system, no energy or matter can flow in or out, so the internal energy cannot change.

7.1

a) For a van der Waals gas, the work done is

$$\delta w_{vdW} = -PdV$$
$$w_{vdW} = -\int_{V_1}^{V_2} PdV = -\int_{V_1}^{V_2}\frac{RT}{V-b} - \frac{a}{V^2}dV$$
$$= RT\ln\left(\frac{V_1 - b}{V_2 - b}\right) + a\left(\frac{1}{V_1} - \frac{1}{V_2}\right)$$

b) For an ideal gas, the work done is

$$\delta w_{ideal} = -PdV$$

$$w_{ideal} = -\int_{V_1}^{V_2} PdV = -\int_{V_1}^{V_2} \frac{RT}{V} dV$$

$$= RT \ln\left(\frac{V_1}{V_2}\right)$$

If we are compressing the gas, then $V_1 > V_2$, so

$$\ln\left(\frac{V_1 - b}{V_2 - b}\right) < \ln\left(\frac{V_1}{V_2}\right)$$

$$a\left(\frac{1}{V_1} - \frac{1}{V_2}\right) > 0$$

Thus we need to delve a little deeper to see which type of gas requires more work to compress. When the gas is less dense, the volume is large, and the logarithmic term dominates. Since the logarithmic term for the van der Waals gas' expansion is less than that for the ideal gas, at the low density limit it takes less work to compress a van der Waals gas. When the density is high, the volume is low, so the *1/V* term is dominant, and thus the van der Waals gas requires more work to compress.

7.3

a) Here, we are considering change in volume (freezing) of water under constant (atmospheric) pressure. So the work is given by

$$\delta w = -PdV$$

$$w = -\int_{V_1}^{V_2} PdV = -P(V_2 - V_1)$$

We thus need to know the volume of the water before and after freezing. Since we are given the initial volume, and the densities before and after freezing, this is a simple calculation.

$$V_1 = (2cm)^3 = 8cm^3 = 8 \times 10^{-6} m^3$$

$$m1 = m2 = m = (2cm)^3 1.000 \, {}^{g}/_{cm^3} = 8g$$

$$V_2 = \frac{m}{0.915 \, {}^{g}/_{cm^3}} = 8.743cm^3 = 8.743 \times 10^{-6} m^3$$

Now it is a simple matter of plugging into the formula, and calculating out the result. Recall that 1 atm is 101 325 Pa, a Pascal is a Newton per meter squared, and that a Joule is a Newton meter.

$$w = -(1atm)\left(8.743 \times 10^{-6} m^3 - 8 \times 10^{-6} m^3\right)$$

$$= -\left(101325 \, {}^{N}/_{m^2}\right)\left(8.743 \times 10^{-6} m^3 - 8 \times 10^{-6} m^3\right)$$

$$= -0.074J$$

b) This is work done by the expansion of the water into ice, so *0.074J* of work is done by the system, or *-0.074J* of work is done on the system.

7.4

a) We start with the equation for differential entropy.

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \sum \frac{\mu_j}{T}dN_j$$

For dependence on V, assume $dU=dN_j=0$. Also $P = \frac{\eta RT}{V}$ for an ideal gas.

$$dS = \frac{P}{T}dV = \frac{\eta k}{V}dV$$

$$\Delta S = \int_{V_1}^{V_2} \frac{\eta k}{V}dV = \eta k \ln\left(\frac{V_2}{V_1}\right)$$

b) For the volume doubling, the entropy change is

$$\Delta S = \eta k \ln\left(\frac{2}{1}\right) = -0.69\eta k$$

7.5

From 7.1, we have

$$w = \eta RT \ln\left(\frac{V_1}{V_2}\right)$$

$$= \eta RT \ln\left(\frac{1}{2}\right) = -0.69\eta RT$$

7.7 Here will we assume that we are dealing with an ideal gas.

Step 1 – Constant volume

$$\delta w_1 = -PdV$$

There is no volume change, so $w_1=0$.

Step 2 – Constant pressure

$$\delta w_2 = -PdV$$

$$w_2 = -\int_{V_1}^{V_2} PdV = -P(V_2 - V_1)$$

$$= -(300atm)(2cm^3 - 1cm^3)$$

$$= -\left(300 * 101325 \,{}^{N}\!/_{m^2}\right)\left(1\times10^{-6} m^3\right)$$

$$= -30.4J$$

Step 3

Again, there is no volume change, so $w_3=0$.

Step 4

$$\delta w_2 = -PdV$$

$$w_2 = -\int_{V_1}^{V_2} PdV = -P(V_2 - V_1)$$

$$= -(100atm)(1cm^3 - 2cm^3)$$

$$= -\left(100 * 101325 \,{}^{N}\!/_{m^2}\right)\left(-1\times10^{-6} m^3\right)$$

$$= 10.1J$$

So,

$$w_{net} = w_1 + w_2 + w_3 + w_4$$

$$= 0 - 30.4J + 0 + 10.1J$$

$$= -20.3J$$

This means that 20.3J of work is done by the system.

7.8

For a Carnot engine, the efficiency η is given by $\eta \le 1 - \frac{T_c}{T_h}$.

a) for $T_h = 380$K and $T_c = 273$K

$$\eta \le 1 - \frac{273}{380}$$

$$\le 0.282$$

b) for $T_h = 380$K and $T_c = 323$K

$$\eta \le 1 - \frac{323}{380}$$

$$\le 0.15$$