Problem Set #11
Assigned November 15, 2013 – Due Friday, November 22, 2013
Please show all work for credit

Colligative properties   Engel Ch. 8:

1. **P8.7**) Assume that 1-bromobutane and 1-chlorobutane form an ideal solution. At 273 K, $P_{chloro}^* = 3790$ Pa and $P_{bromo}^* = 1394$ Pa. When only a trace of liquid is present at 273 K, $y_{chloro} = 0.75$.

a. Calculate the total pressure above the solution.

b. Calculate the mole fraction of 1-chlorobutane in the solution.

c. What value would Z_{chloro} have in order for there to be 4.86 mol of liquid and 3.21 mol of gas at a total pressure equal to that in part (a)? [*Note*: This composition is different from that of part (a).]

a) Calculate the total pressure above the solution.

$$y_{chloro} = \frac{P_{chloro}^* P_{total} - P_{chloro}^* P_{bromo}^*}{P_{total}\left(P_{chloro}^* - P_{bromo}^*\right)}$$

$$0.75 = \frac{3790 \text{ Pa} \times P_{total} - 3790 \text{ Pa} \times 1394 \text{ Pa}}{P_{total} \times (3790 \text{ Pa} - 1394 \text{ Pa})}$$

$$P_{total} = \frac{3790 \text{ Pa} \times 1394 \text{ Pa}}{3790 \text{ Pa} - 0.75 \times (3790 \text{ Pa} - 1394 \text{ Pa})} = 2651 \text{ Pa}$$

b) Calculate the mole fraction of 1-chlorobutane in the solution.

$$P_{total} = x_{chloro} P_{chloro}^* + (1 - x_{chloro}) P_{bromo}^*$$

$$x_{chloro} = \frac{P_{total} - P_{bromo}^*}{P_{chloro}^* - P_{bromo}^*} = \frac{2651 \text{ Pa} - 1394 \text{ Pa}}{3790 \text{ Pa} - 1394 \text{ Pa}} = 0.525$$

c) What value would Z_{chloro} have in order that there are 4.86 moles of liquid and 3.21 moles of gas at a total pressure equal to that in part a)? (This composition is different than that in part a.)

$$y_{chloro} = \frac{P_{chloro}^* P_{total} - P_{chloro}^* P_{bromo}^*}{P_{total}\left(P_{chloro}^* - P_{bromo}^*\right)}$$

$$= \frac{3790 \text{ Pa} \times 2651 \text{ Pa} - 3790 \text{ Pa} \times 1394 \text{ Pa}}{2651 \text{ Pa} \times (3790 \text{ Pa} - 1394 \text{ Pa})} = 0.750$$

$$x_{chloro} = \frac{y_{chloro} P_{bromo}^*}{P_{chloro}^* + (P_{bromo}^* - P_{chloro}^*) y_{chloro}}$$

$$= \frac{0.750 \times 1394 \text{ Pa}}{3790 \text{ Pa} + (1394 \text{ Pa} - 3790 \text{ Pa}) \times 0.750} = 0.525$$

$$n_{liq}^{tot}\left(Z_{chloro} - x_{chloro}\right) = n_{vapor}^{tot}\left(y_{chloro} - Z_{chloro}\right)$$

$$Z_{chloro} = \frac{n_{vapor}^{tot} y_{chloro} + n_{liq}^{tot} x_{chloro}}{n_{vapor}^{tot} + n_{liq}^{tot}} = \frac{3.21 \text{ mol} \times 0.750 + 4.86 \text{ mol} \times 0.525}{3.21 \text{ mol} + 4.86 \text{ mol}} = 0.614$$

2. P8.14) Ratcliffe and Chao [*Canadian Journal of Chemical Engineering* 47 (1969), 148] obtained the following tabulated results for the variation of the total pressure above a solution of isopropanol ($P_1^* = 1008$ Torr) and *n*-decane ($P_2^* = 48.3$ Torr) as a function of the mole fraction of the *n*-decane in the solution and vapor phases. Using these data, calculate the activity coefficients for both components using a Raoult's law standard state.

P (Torr)	x_2	y_2
942.6	0.1312	0.0243
909.6	0.2040	0.0300
883.3	0.2714	0.0342
868.4	0.3360	0.0362
830.2	0.4425	0.0411
786.8	0.5578	0.0451
758.7	0.6036	0.0489

a) for isoproponal $P_1^* = 1008$ Torr

for *n*-decane $P_2^* = 48.3$ Torr

Using the relations $P_i = y_i P_{total}$, $a_i = P_i / P_i^*$, and $\gamma_i = \dfrac{a_i}{x_i}$, the calculated activities and activity

coefficients are shown below.

P(Torr)	x_2	y_2	a_1	a_2	γ_1	γ_2
942.6	0.1312	0.0243	0.912	0.474	1.05	3.61
909.6	0.2040	0.0300	0.875	0.565	1.10	2.77
883.3	0.2714	0.0342	0.846	0.625	1.16	2.30
868.4	0.3360	0.0362	0.831	0.651	1.25	1.94
830.2	0.4425	0.0411	0.790	0.706	1.42	1.60
786.8	0.5578	0.0451	0.745	0.735	1.69	1.32
758.7	0.6036	0.0489	0.716	0.768	1.81	1.27

3. P8.33) When a solute shows very small activity coefficients at relatively low concentrations, this is evidence for strong interactions between the solute molecules. For example, the activity coefficient for 6-methylpurine is 0.329 at 0.20 m, whereas the activity coefficient of cytidine is more than twice that value at a comparable concentration. This is an indication that 6-methylpurine may be aggregating.

The simplest form of aggregation is dimer formation. If M forms a dimer D in solution we have the equilibrium: $2M \rightleftarrows D$. Assume the equilibrium constant is $K = \dfrac{C_D}{C_M^2}$ where C_D is the concentration of dimer, C_M is the concentration of monomer and $C_T = 2 C_D + C_M$. The chemical potential for the monomer is $\mu_M = \mu_M^0 + RT \ln C_M$ Dimerization can be treated as a type of non-ideality where $\mu_M = \mu_M^0 + RT \ln \gamma C_T$ where the activity coefficient $\gamma = 1$ if no dimer forms and $\gamma < 1$ if a dimer forms.

a. Using the two equations for the chemical potential of M, given above, obtain an expression for the activity coefficient γ in terms of C_M and C_T.

b. Using the expression for the equilibrium constant K and your result from part a show that

$$\gamma = \frac{\left(1 + 8KC_T\right)^{1/2}}{4KC_T} - \frac{1}{4KC_T}$$

c. Using the data given above, calculate the equilibrium constant for the dimerization of 6-methylpurine. Estimate the equilibrium constant for the dimerization of cytidine.

a) Combining the two equations yields:

$$\mu_M^{\circ} + R\,T\ln\left(C_M\right) = \mu_M^{\circ} + R\,T\ln\left(\gamma C_T\right)$$

Then:

$$\ln\left(C_M\right) = \ln\left(\gamma C_T\right) = \ln(\gamma) + \ln\left(C_T\right)$$

$$\ln(\gamma) = \ln\left(C_M\right) - \ln\left(C_T\right) \quad \rightarrow \quad \gamma = \frac{C_M}{C_T}$$

b) Combining the equations for K, C_T, and part a we obtain:

$$K = \frac{C_D}{C_M{}^2} = \frac{\left(C_T/2 - C_M/2\right)}{C_M{}^2} = \frac{C_T}{2C_M{}^2} - \frac{1}{2C_M}$$

$$2C_M{}^2 K = C_T - 2C_M \quad \rightarrow \quad 2C_M{}^2 K + 2C_M - C_T = 0$$

$$C_M{}^2 + \frac{C_M}{K} - \frac{C_T}{2K} = 0$$

Solving the quadratic equation for C_M yields:

$$C_M = \frac{\sqrt{1 + 8\,C_T K} - 1}{4\,K}$$

Then γ can be expressed as:

$$\gamma = \frac{C_M}{C_T} = \frac{\sqrt{1 + 8\,C_T K} - 1}{4\,K\,C_T} = \frac{\sqrt{1 + 8\,C_T K}}{4\,K\,C_T} - \frac{1}{4\,K\,C_T}$$

c) We obtain the equilibrium constant for 6-methylpurine by solving for K:

$$\gamma = \frac{\left(1 + 8KC_T\right)^{1/2}}{4KC_T} - \frac{1}{4KC_T}$$

$$K = \frac{\left(1 - \gamma\right)}{\left(2\,C_T\,\gamma^2\right)} = \frac{\left(1 - 0.329\right)}{\left(2\,(0.2\,M) \times (0.329)^2\right)} = 15.1$$

And in analogy for cytidine with two times the activity coefficient:

$$K = \frac{\left(1 - \gamma\right)}{\left(2\,C_T\,\gamma^2\right)} = \frac{\left(1 - 0.658\right)}{\left(2\,(0.2\,M) \times (0.658)^2\right)} = 2.0$$

4.

P8.38) When the cells of the skeletal vacuole of a frog were placed in a series of NaCl solutions of different concentrations at 298 K, it was found that the cells remained unchanged in a 0.70 % (by weight) NaCl solution. For a 0.70 % NaCl solution the freezing point is depressed by –0.406 K. What is the osmotic pressure of the cell cytoplasm at $T = 298$ K?

We obtain the osmotic pressure by combining:

$$\pi = \frac{n_{solute}RT}{V} \text{ and } m_{solute} = \frac{\Delta T_f}{-K_f} \text{ from } \Delta T_f = -K_f m_{solute}$$

$$\pi = \frac{n_{solute}RT}{V} = \frac{\left(\frac{\Delta T_f}{-K_f}\right)RT}{1/\rho} = \frac{\left(\frac{(-0.406\ K)}{(-1.86\ K\ kg\ mol^{-1})}\right) \times (8.314472\ J\ K^{-1}\ mol^{-1}) \times (298\ K)}{(0.001\ L\ kg^{-1})}$$

$$= 540834.1\ Pa = 5.34\ atm$$

5. **P8.41)** The following data on the osmotic pressure of solutions of bovine serum albumin were obtained from the work of Scatchard et al., *J. American Chemical Society 68* (1946), 2320:

Concentration (g L^{-1})	27.28	56.20	8.95	17.69
Osmotic Pressure (mmHg)	8.35	19.33	2.51	5.07

Calculate the molecular weight of bovine serum albumin. Assume $T = 298$ K.

We need to plot π/C_2 versus C_2:
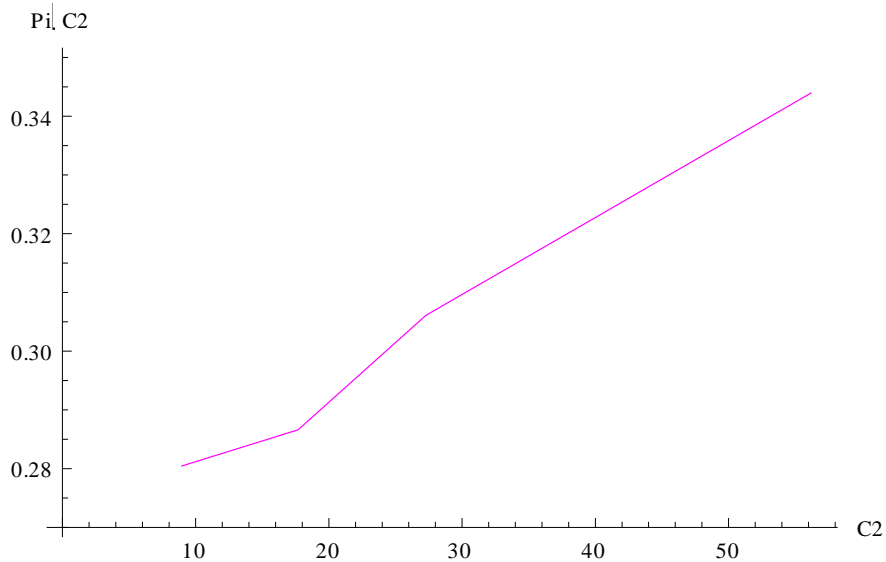
For C2 → 0, $\pi/C_2 \to 0.275$ mmHg g $L^{-1} = 0.0003618$ atm g L^{-1}. The molecular weight is then:

$$M_{solute} = \frac{\lim}{C_2 \to \infty} \frac{RT}{\pi/C_2} = \frac{(0.0821\ L\ atm\ K\ mol^{-1}) \times (298\ K)}{(0.0003618\ atm\ g\ L-1)} = 67622.4\ g\ mol^{-1}$$

6. **P8.45)** The concentrations in moles per kilogram of water for the dominant salts in sea water are:

Ion	Cl^-	Na^+	Mg^{2+}	SO_4^{2-}	Ca^{2+}
Mol kg^{-1}	0.546	0.456	0.053	0.028	0.010

Calculate the osmotic pressure exerted by sea water at $T = 298$ K. Suppose sea water is separated from pure water by a membrane that is permeable to water but impermeable to the ions in sea water. Assuming the density of sea water is about equal to pure water at $T = 298$ K, calculate the column of sea water that would be supported by osmotic pressure.

To calculate can assume 1 kg of sea water is 1 L, sum the ion concentrations, the osmotic pressure is:

$$\pi = \frac{n_{solutes}RT}{V} = \frac{(0.546+0.456+0.053+0.028+0.010)\,mol \times (8.314472\,J\,K\,mol^{-1}) \times (298\,K)}{(0.001\,m^3)}$$

$= 2708139.93\,Pa = 27.08\,bar$

The column of sea water that would be supported by this osmotic pressure can be calculated as follows:

$\pi = p = 1\,atm + \rho g h$

$$h = \frac{(\pi - 1\,atm)}{\rho g} = \frac{(2708139.93\,Pa - 101325\,Pa)}{(1000\,kg\,m^{-3}) \times (9.81\,m\,s^{-2})} = 265.73\,m = 0.266\,km$$

> Note how huge this is, for ~0.5 M solution, means can use osmotic pressure for small concentrations or macromolecules
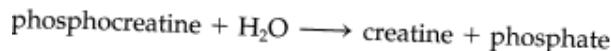
Equilibria Ch. 4:

7. **P4.2)** − In the frog muscle rectus abdominis, the concentration of ATP, ADP, and phosphate are 1.25E-3M, 0.50E-3M, and 2.5E-3M, respectively.

a) Calculate the Gibbs free-energy change ΔG° for the hydrolysis of ATP in muscle. Take the temperature and pH of the muscle as $25\,^{\circ}C$ and 7, respectively.

b) For the muscle described, what is the maximum amount of mechanical work it can do per mole of ATP hydrolyzed?

c) In muscle, the enzyme creatine phosphokinase catalyzes the following reaction:

$$\text{phosphocreatine + ADP} \longrightarrow \text{creatine + ATP}$$

The standard Gibbs free-energy of hydrolysis of phosphocreatine at $25\,^{\circ}C$ and pH7 is -43.1kJ/mol:

$$\text{phosphocreatine + H}_2\text{O} \longrightarrow \text{creatine + phosphate}$$

Calculate the equilibrium constant of the creatine phosphokinase reaction.
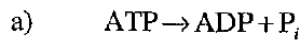
a) $ATP \rightarrow ADP + P_i$
(Eq. 4.15)
$\Delta G' = \Delta G^{\circ\prime} + RT\,\ln([ADP][P_i]/[ATP])$

$= -31.00 + (8.314 \times 10^{-3})(298)\ln\left[(0.50 \times 10^{-3})(2.5\,x\,10^{-3})/(1.25 \times 10^{-3})\right]$

$= -31.0 - 17.1$

$= \underline{-48.1\,kJ\,mol^{-1}}$

b) $-w_{max,\,rev} = \Delta G' = \underline{48.1\,kJ\,mol^{-1}}$ (Eq. 4.55)

> Note this sign is tricky. Work done by system is negative, but max work a system can do is a positive concept.

c) $\Delta G^{\circ\prime}\ (kJ\,mol^{-1})$

$PC + H_2O \rightarrow C + P_i$;   -43.1
$P_i + ADP \rightarrow ATP + H_2O$;   31.0
$PC + ADP \rightarrow C + ATP$;   −12.1
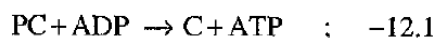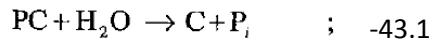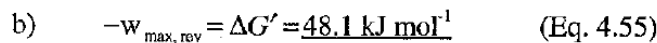
$\ln K = -\Delta G^{\circ\prime}/RT = 12,000/(8.314)(298) = 4.88$
$K = \underline{132}$

8. P4.5)

5. The following reactions can be coupled to give alanine and oxaloacetate:

glutamate + pyruvate $\rightleftharpoons$ ketoglutarate + alanine

($\Delta G_{303}^{0\prime} = -1004\ \text{J mol}^{-1}$)

glutamate + oxaloacetate $\rightleftharpoons$
ketoglutarate + aspartate

($\Delta G_{303}^{0\prime} = -4812\ \text{J mol}^{-1}$)

(a) Write the form of the equilibrium constant for the reaction

pyruvate + aspartate $\rightleftharpoons$ alanine + oxaloacetate

and calculate the numerical value of the equilibrium constant at 30°C.

(b) In the cytoplasm of a certain cell, the components are at the following concentrations: pyruvate = 10^{-2} M, aspartate = 10^{-2} M, alanine = 10^{-4} M, and oxalo-acetate = 10^{-5} M. Calculate the Gibbs free-energy change for the reaction of part (a) under these condi-tions. What conclusion can you reach about the direc-tion of this reaction under cytoplasmic conditions?

$$\Delta G_{303}^{o\prime}\ (\text{J mol}^{-1})$$

Glu + Pyr $\longleftrightarrow$ Ket + Ala ;	−1004
Ket + Asp $\longleftrightarrow$ Glu + Ox ;	4812
Pyr + Asp $\longleftrightarrow$ Ala + Ox ;	3808

a) $K = [\text{Ala}][\text{Ox}]/[\text{Pyr}][\text{Asp}]$

$\ln K = -\Delta G_{303}^{o\prime}/RT = -3808/(8.314)(303) = -1.51$

$K = \underline{0.22}$

b) $\Delta G_{303}^{\prime} = \Delta G_{303}^{o\prime} + RT\ \ln[(10^{-4})(10^{-5})/(10^{-2})(10^{-2})]$

$= 3808 + (8.314)(303)(-11.5) = \underline{-25,200\ \text{J mol}^{-1}}$

The reaction proceeds in the forward direction under cytoplasmic conditions.

9. P4.14)

You made a pH 9.0 buffer solution at 25°C by mixing NaOH and histidine (HisH) to give a solution that is 0.200 M in total concentration of histidine.

(a) Calculate the concentrations of all species at 25°C.

(b) What is the pH of the buffer at 40°C? The two most important ΔH^{0} values for histidine are given in table 4.2; assume that $\Delta H^{0} = 0$ for the first ionization. You can ignore the volume change of the solution.

(c) Calculate the concentrations of all species at 40°C.

a) $pK_1 = 1.82;\ pK_2 = 6.00;\ pK_3 = 9.16$

at pH 9.0 HisH and His$^-$ are principal species

$K_3 = \dfrac{[\text{His}^-][\text{H}^+]}{\text{HisH}}$

$\dfrac{[\text{His}^-][\text{H}^+]}{\text{HisH}} = \dfrac{10^{-9.16}}{10^{-9.00}} = 0.6918$

$[\text{His}^-] + [\text{HisH}] = 0.200$

$0.6918[\text{HisH}] + [\text{HisH}] = \underline{0.200}$

$[\text{HisH}] = 0.200/1.6918 = \underline{0.118\,\text{M}}$

$[\text{His}^-] = \underline{0.082\,\text{M}}$

$K_2 = \dfrac{[\text{HisH}][\text{H}^+]}{[\text{His}^+]} = 10^{-6.00}$

$[\text{His}^+] = \dfrac{(0.118)(10^9)}{(10^{-6})} = 1.18 \times 10^{-4}\,\text{M}$

$[\text{His}^{2+}] = \dfrac{(\text{His}^+)(\text{H}^+)}{(10^{-1.82})} = \dfrac{(1.18 \times 10^{-4})(10^{-9})}{(10^{-1.82})} = 7.80 \times 10^{-12}\,\text{M}$

$[\text{OH}^-] = \text{Kw}/10^{-9} = 10^{-5}\,\text{M}$

$[\text{Na}^+] = [\text{His}^-] + [\text{OH}^-] - [\text{H}^+] - [\text{His}^+] - 2[\text{His}^{2+}]$

$[\text{Na}^+] = \underline{0.082\text{M}}$

b) $\Delta H_1 = 0;\ \Delta H_2 = 29.9\ \text{kJ mol}^{-1};\ \Delta H_3 = 43.6\ \text{kJ mol}^{-1}$

$\ln\left[\dfrac{K(40°\text{C})}{K(25°\text{C})}\right] = \dfrac{-\Delta H°}{R}\left(\dfrac{1}{313} - \dfrac{1}{298}\right) = (0.01934)(\Delta H°\ \text{in kJ})$

$K_1 = 10^{-1.82};\ K_2 = 1.78 \times 10^{-6};\ K_3 = 2.32 \times 10^{-9.16}$

$\Delta H_w = 55.84\ \text{kJ mol}^{-1}\quad \text{Kw} = 2.94 \times 10^{-14}$

$K_3 = \dfrac{[\text{His}^-][\text{H}^+]}{\text{HisH}}$ this equilibrium predominates at pH 9

$\text{Kw} = [\text{H}^+][\text{OH}^-]$

$[\text{Na}^+] \cong [\text{His}^-]$ because other charged species are small

$[\text{His}^-] + [\text{HisH}] = 0.200$

$[\text{Na}^+] = 0.082\ \text{M}$ because no volume change

$[\text{His}^-] = 0.082\ \text{M}$

$[\text{HisH}] = 0.118\ \text{M}$

$[\text{H}^+] = (0.118/0.082)K_3 = 2.31 \times 10^{-9}\ \text{M}$

$\text{pH} = \underline{8.64}$

c) $[\text{His}^+] = \dfrac{(0.118)(2.31 \times 10^{-9})}{(1.78 \times 10^{-6})}$

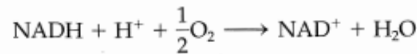$[\text{His}^{2+}] = \underline{1.53 \times 10^{-4}\ \text{M}}$

$[\text{His}^{2+}] = \dfrac{(1.53 \times 10^{-4})(2.31 \times 10^{-9})}{(10^{-1.82})}$

$[\text{His}^+] = \underline{2.33 \times 10^{-11}\ \text{M}}$

$[\text{OH}^-] = (2.94 \times 10^{-4})/(2.31 \times 10^{-9}) = \underline{1.27 \times 10^{-5}\ \text{M}}$

10. P4.27)

In the presence of oxygen, most living cells make ATP by oxidative phosphorylation, which takes place in mitochondria. One of the major substrates that is oxidized is NADH. The overall reaction for this energy-yielding process is

$$\text{NADH} + \text{H}^+ + \frac{1}{2}\text{O}_2 \longrightarrow \text{NAD}^+ + \text{H}_2\text{O}$$

(a) Use table 4.1 to calculate the Gibbs free-energy change of the above reaction as it takes place in mitochondria at pH 7 and 25°C. The concentrations of reactants and products are [NADH] = 1 mM, [NAD$^+$] = 2 mM, and P_{O_2} = 0.1 atm.

(b) Given that 3 mol of ATP is made from P$_i$ and ADP for every mole of NADH oxidized, what fraction of the Gibbs free-energy change of part (a) is used in making ATP in mitochondria during oxidative phosphorylation? [ADP] = 1 mM, [ATP] = 3 mM, and P$_i$ = 10 mM.

a) $\text{NAD}^+ + \text{H}^+ + 2e^- + \text{NADH};\quad E° = -0.320\ \text{V}$

b) $1/2\text{O}_2 + 2\text{H}^+ + 2e^- + 2\text{H}_2\text{O};\quad E°' = 0.816\ \text{V}$

$\text{NADH} + \text{H}^+ + 1/2\text{O}_2 + \text{NAD}^+ + \text{H}_2\text{O};\quad E°' = 1.136\ \text{V}$

$\Delta G°' = -96.485(2)(1.136) = -219.2\ \text{kJ mol}^{-1}$

$\Delta G' = \Delta G°' + RT\ln([\text{NAD}^+]/[\text{NADH}][\text{O}_2]^{1/2})$

$\quad = -219{,}214 + (8.314)(298)\ln[(2 \times 10^{-3})/(1 \times 10^{-3})(0.1)^{1/2}]$

$\quad = \underline{-214.6\ \text{kJ mol}^{-1}}$

b) $\Delta G' = 3\Delta \overline{G}°' + 3RT\ln[\text{ATP}]/([\text{ADP}][\text{P}_i])$

$\quad = 3(31{,}000) + 3(8.314)(298)\ln[(3 \times 10^{-3})/(1 \times 10^{-3})(10 \times 10^{-3})]$

$\quad = 93{,}000 + 42{,}400 = \underline{135.4\ \text{kJ mol}^{-1}}$

Fractional conversion to ATP = $135.4/214.6 = \underline{0.63}$

Use the $\Delta G° = -219$ kJ/mol, as provided to you by e-mail, directly to get ΔG. This shows it can be derived from electrochemistry

This answer assume biological standard state, pH7

Ionic equilibria Engel Ch. 9:

11. P9.2) Calculate $\Delta H^\circ_{reaction}$ and $\Delta G^\circ_{reaction}$ for the reaction

$$Ba(NO_3)_2(aq) + 2KCl(aq) \rightarrow BaCl_2(s) + 2KNO_3(aq).$$
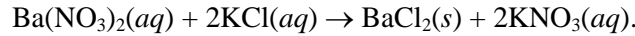
$\Delta G^\circ_{reaction} = \Delta G^\circ_f (BaCl_2, s) + 2\,\Delta G^\circ_f (K^+, aq) + 2\,\Delta G^\circ_f (NO_3^-, aq) - \Delta G^\circ_f (Ba^{2+}, aq)$

$\qquad -2\,\Delta G^\circ_f (NO_3^-, aq) - 2\,\Delta G^\circ_f (K^+, aq) - 2\,\Delta G^\circ_f (Cl^-, aq)$

$\Delta G^\circ_{reaction} = \Delta G^\circ_f (BaCl_2, s) - \Delta G^\circ_f (Ba^{2+}, aq) - 2\,\Delta G^\circ_f (Cl^-, aq)$

$\Delta G^\circ_{reaction} = -806.7 \text{ kJ mol}^{-1} + 560.8 \text{ kJ mol}^{-1} + 2 \times 131.2 \text{ kJ mol}^{-1} = 16.5 \text{ kJ mol}^{-1}$

$\Delta H^\circ_{reaction} = \Delta H^\circ_f (BaCl_2, s) - \Delta H^\circ_f (Ba^{2+}, aq) - 2\,\Delta H^\circ_f (Cl^-, aq)$

$\Delta H^\circ_{reaction} = -855.0 \text{ kJ mol}^{-1} + 537.6 \text{ kJ mol}^{-1} + 2 \times 167.2 \text{ kJ mol}^{-1} = 17 \text{ kJ mol}^{-1}$

12. P9.12) Calculate the mean ionic molality and mean ionic activity of a 0.150 m $Ca(NO_3)_2$ solution for which the mean ionic activity coefficient is 0.165.

$$m_\pm = \left(v_+^{v_+} v_-^{v_-}\right)^{1/v} m = \left(2^2\right)^{1/3} 0.150 \text{ mol kg}^{-1} = 0.238 \text{ mol kg}^{-1}$$

$$a_\pm = \left(\frac{m_\pm}{m^\circ}\right) \gamma_\pm = 0.238 \times 0.165 = 0.0393$$

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13. P5.6)

In living biological cells, the concentration of sodium ions inside the cell is kept at a lower concentration than the concentration outside the cell, because sodium ions are actively transported from the cell.

(a) Consider the following process at 37°C and 1 atm.

1 mol NaCl(0.05 M inside) $\longrightarrow$

$\qquad\qquad$ 1 mol NaCl(0.20 M outside)

Write an expression for the free-energy change for this process in terms of activities. Define all symbols used.

(b) Calculate $\Delta\mu$ for the process. You may approximate the activities by concentrations in M. Will the process proceed spontaneously?

(c) Calculate ΔG for moving 3 mol of NaCl from inside to outside under these conditions.

(d) Calculate $\Delta\mu$ for the process if the activity of NaCl inside is equal to that outside.

(e) Calculate $\Delta\mu$ for the process at equilibrium.

(f) The standard free energy for hydrolysis of ATP to ADP (ATP + $H_2O \rightarrow$ ADP + phosphate) in solution is $\Delta G^0 = -31.3$ kJ mol^{-1} at 37°C, 1 atm. The free energy of this reaction can be used to power the sodium-ion pump. For a ratio of ATP to ADP of 10, what must be the concentration of phosphate to obtain -40 kJ mol^{-1} for the hydrolysis? Assume that activity coefficients are 1 for the calculation.

(g) If the ratio of ATP to ADP is 10, what is the concentration of phosphate at equilibrium? Assume ideal solution behavior. What do you conclude from your answer?

a) $\Delta\bar{G} = RT \ln (a_{outside}/a_{inside})$ (Eq. 5.25)

a = activity of NaCl (either inside or outside), but with the same standard

$\Delta\bar{G}$ = free energy change to transport 1 mol NaCl.

b) $\Delta\mu = RT\ln \dfrac{0.20}{0.05} = \underline{3573 \text{ J}}$. Not spontaneous.

c) $\Delta G = 3\Delta\bar{G}$ (from b) = $\underline{10719 \text{ J}}$.

d) $\Delta\mu = 0$

e) $\Delta\mu = 0$

f) $\Delta G = \Delta G^\circ + RT \ln \dfrac{[ADP][P]}{[ATP]}$

$-40 = -31 + (10^{-3})(8.314)(310) \ln \dfrac{(1)[P]}{10}$

$\ln \dfrac{[P]}{10} = -3.49$

$[P] = \underline{0.30 \text{ M}}$

g) $K' = e^{-\Delta G^\circ/RT} = 1.67 \times 10^5 = \dfrac{[ADP][P]}{[ATP]}$

$[P] = \underline{1.67 \times 10^6 \text{ M}}$ It is clear that equilibrium cannot be attai

14. P5.18)

(a) Assuming that glucose and water form an ideal solution, what is the equilibrium vapor pressure at 20°C of a solution of 1.00 g of glucose (mol wt 180) in 100 g of water? The vapor pressure of pure water is 17.54 torr at 20°C.

(b) What is the osmotic pressure, in torr, of the solution in part (a) versus pure water?

(c) What is the activity of water as a solvent in such a solution?

(d) What would be the osmotic pressure versus pure water of a solution containing both 1.00 g of glucose and 1.00 g of sucrose (mol wt 342) in 100 g of water at 20°C?

a) $$\frac{P_A^0 - P_A}{P_A^0} = \frac{wt_B}{M_B n_A} = \frac{1.00}{(180)\left(\frac{100}{18}\right)} = 10^{-3}$$

$$P_A^o - P_A = 17.54 \times 10^{-3}$$
$$P_A = 17.52 \text{ torr}$$

b) $$\pi = cRT \quad c \cong \frac{1.00}{(180)(0.1)} = 0.0555 \quad (\text{Eq. 5.58a})$$

$$\pi = (0.0555)(0.08205)(760)(293)$$
$$\pi = 1015 \text{ torr} \ (1.335 \text{ atm})$$

c) $$\ln a_A = \frac{-\pi \overline{V}_A}{RT} = \frac{(1.335)(18)}{(82.05)(293)} = 0.999$$

d) Osmotic pressure gives a number average molecular weight, $\overline{M}_n$. Therefore Eq. (5.54) can be written as

$$\pi = wRT / \overline{M}_n \quad w = \text{cong in g}l^{-1} \cong 20 \quad (\text{Eq. 5.59})$$

$$\overline{M}_n = \frac{n_1 M_1 + n_2 M_2}{n_1 + n_2} = \frac{2}{\frac{1}{180} + \frac{1}{342}} = 236$$

$$\pi = \frac{(20)(0.08205)(760)(293)}{236} = 1548 \text{ torr}$$

Extras (good for test)
Engel Ch. 8:

15. P8.2) A volume of 5.50 L of air is bubbled through liquid toluene at 298 K, thus reducing the mass of toluene in the beaker by 2.38 g. Assuming that the air emerging from the beaker is saturated with toluene, determine the vapor pressure of toluene at this temperature.

$$P = \frac{nRT}{V} = \frac{2.38 \text{ g} \times \frac{1 \text{ mol}}{92.14\text{g mol}^{-1}} \times 0.08314 \text{ L bar K}^{-1} \times 298 \text{ K}}{5.50 \text{ L}} = 0.116 \text{ bar}$$

16. P8.22) A sample of glucose ($C_6H_{12}O_6$) of mass 1.25 g is placed in a test tube of radius 1.00 cm. The bottom of the test tube is a membrane that is semipermeable to water. The tube is partially immersed in a beaker of water at 298 K so that the bottom of the test tube is only slightly below the level of the water in the beaker. The density of water at this temperature is 997 kg m^{-3}. After equilibrium is reached, how high is the water level of the water in the tube above that in the beaker? What is the value of the osmotic pressure?

You may find the approximation $\ln (1/1 + x) \approx -x$ useful.

$$\pi V_m^* + RT \ln x_{solvent} = \pi V_m^* + RT \ln \frac{n_{sucrose}}{n_{solvent} + n_{sucrose}} = 0$$

$$\rho g h V_m^* + RT \ln \frac{\frac{\rho A h}{M}}{\frac{\rho A h}{M} + n_{sucrose}} = \rho g h V_m^* + RT \ln \frac{1}{1 + \frac{n_{sucrose} M}{\rho A h}} = 0$$

Expanding the argument of the logarithmic term in a Taylor series, $\ln \frac{1}{1+x} \approx -x$

$$\rho g h V_m^* - RT \frac{n_{sucrose} M}{\rho A h} = 0$$

$$h = \sqrt{\frac{RT n_{sucrose} M}{\rho^2 A g V_m^*}} = \sqrt{\frac{RT n_{sucrose}}{\rho A g}}$$

$$= \sqrt{\frac{8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 298 \text{ K} \times \frac{1.25 \times 10^{-3}\text{kg}}{0.18016 \text{ kg mol}^{-1}}}{997 \text{ kg m}^{-3} \times 3.14 \times 10^{-4}\text{m}^2 \times 9.81 \text{ m s}^{-2}}} = 2.37 \text{ m}$$

$$\pi = \rho g h = 997 \text{ kg m}^{-3} \times 9.81 \text{ m s}^{-2} \times 2.37 \text{ m} = 2.32 \times 10^4 \text{Pa}$$

17. P8.24) To extend the safe diving limit, both oxygen and nitrogen must be reduced in the breathing mixture. One way to do this is to mix oxygen with helium. Assume a mixture of 10.% oxygen and 90.% helium. Assuming Henry's law behavior, calculate the levels of oxygen and helium in the blood of a diver at 100 m. Assume $T = 298$ K.

The pressure at a 100 m is given by:

$$p(100 \text{ m}) = 1 \text{ atm} + \rho \text{ g h} = (1 \text{ atm}) + (1000 \text{ kg m}^{-3}) \times (9.81 \text{ m s}^{-2}) \times (100.0 \text{ m})$$

$$= (101325 \text{ Pa}) + (981000 \text{ Pa}) = 1082325 \text{ Pa}$$

For a mixture of 10% O_2:

$$p_{O_2} = (0.1) \times (1082325 \text{ Pa}) = 108232.5 \text{ Pa}$$

Using Henry's Law:

$$x_{O_2} = \frac{p_{O_2}}{k_{k,O_2}} = \frac{(108232.5 \text{ Pa})}{(4.95 \times 10^4 \text{ bar}) \times (1.00 \times 10^5 \text{ bar}^{-1} \text{ Pa})} = 2.1865 \times 10^{-5}$$

Now we can us the molar volume of water:

$$x_{O_2} \approx \frac{n_{O_2}}{V_{H_2O}} V_{m,H_2O}$$

Then the concentration is:

$$\frac{x_{O_2}}{V_{m,H_2O}} = \frac{n_{O_2}}{V_{H_2O}} = \frac{(2.1865 \times 10^{-5} \text{ mol})}{(0.018 \text{ L})} = 1.21 \times 10^{-3} \text{ M}$$

$$C_{O_2} = (1.21 \times 10^{-3} \text{ mol/L}) \times (32000 \text{ mg mol}^{-1}) = 38.72 \text{ mg L}^{-1}$$

Equivalently we obtain for a mixture of 90% He:

$$p_{He} = (0.9) \times (1082325 \text{ Pa}) = 974092.5 \text{ Pa}$$

Using Henry's Law:

$$x_{He} = \frac{p_{He}}{k_{k,He}} = \frac{(974092.5 \text{ Pa})}{(1.49 \times 10^6 \text{ bar}) \times (1.00 \times 10^5 \text{ bar}^{-1} \text{ Pa})} = 6.538 \times 10^{-6}$$

Now we can us the molar volume of water:

$$x_{He} \approx \frac{n_{He}}{V_{H_2O}} V_{m,H_2O}$$

Then the concentration is:

$$\frac{x_{He}}{V_{m,H_2O}} = \frac{n_{He}}{V_{H_2O}} = \frac{(6.538 \times 10^{-6} \text{ mol})}{(0.018 \text{ L})} = 3.63 \times 10^{-4} \text{ M}$$

$$C_{He} = (3.63 \times 10^{-4} \text{ mol/L}) \times (4000 \text{ mg mol}^{-1}) = 1.4 \text{ mg L}^{-1}$$

18. P8.26) The average osmotic pressure of human blood versus water is 7.60 atm. at a temperature of $T = 310.$ K. Calculate the total solute concentration in human blood.

Solving the van't Hoff osmotic equation for n_{solute}/V:

$$\pi = \frac{n_{solute} R T}{V}$$

$$\frac{\pi}{R T} = \frac{n_{solute}}{V} = \frac{(770070 \text{ Pa})}{(8.314472 \text{ J mol}^{-1} \text{ K}^{-1}) \times (310 \text{ K})} = 299 \text{ mol}^{-1} \text{ m}^{-3} = 0.299 \text{ mol}^{-1} \text{ l}^{-1}$$

19. P8.37) Red blood cells do not swell or contract in a solution composed of 103 g of sucrose dissolved in a kilogram of water. Assuming the red blood cell membrane is impermeable to sucrose, calculate the osmotic pressure exerted by the cell cytoplasm at $T = 310$ K relative to pure water. Assume sucrose forms an ideal solution in water.

The Osmotic pressure is given by:

$$\pi = \frac{n_{solute} RT}{V} = \frac{(103 \text{ g} / 342 \text{ g mol}^{-1}) \times (8.314472 \text{ J K mol}^{-1}) \times (310 \text{ K})}{(0.001 \text{ m}^3)} = 776260.5 \text{ Pa} = 7.661 \text{ atm}$$

20. P8.43) Assume an aqueous solution contains equal numbers of polynucleotides with molecular weights of roughly 20,000, 50,000, and 100,000, units of g mol^{-1}. Calculate the osmotic pressure of this solution at $T = 298$ K. Assume 1.00 g of polynucleotide is dissolved in 1.00 L of water.

For equal number of polynucleotides, n, we have:

$$n M_1 + n M_2 + n M_3 = 1 \text{ g}$$

$$n = \frac{1 \text{ g}}{(M_1 + M_2 + M_3)} = \frac{1 \text{ g}}{(20000 + 50000 + 100000) \text{ g mol}^{-1}} = 5.88 \times 10^{-6} \text{mol of each. n(solute,total)} =$$

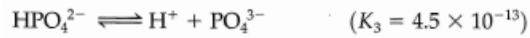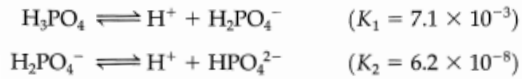$$3 \text{ x } 5.88 \times 10^{-6} \text{mol}$$

Then the Osmotic Pressure is:

$$\pi = \frac{n_{solute} RT}{V} = \frac{3x(5.88 \times 10^{-6} \text{mol}) \times (8.314472 \text{ J K mol}^{-1}) \times (298 \text{ K})}{(0.001 \text{ m}^3)} = 43.70 \text{ Pa} = 0.00043 \text{ atm}$$

21. P9.9) Express $\gamma_\pm$ in terms of γ_+ and γ_- for (a) $SrSO_4$, (b) $MgBr_2$, (c) K_3PO_4, and (d) $Ca(NO_3)_2$. Assume complete dissociation.

a) $SrSO_4$ $\gamma_\pm = \left(\gamma_+\gamma_-\right)^{1/2}$

c) K_3PO_4 $\gamma_\pm = \left(\gamma_+^3\gamma_-\right)^{1/4}$

b) $MgBr_2$ $\gamma_\pm = \left(\gamma_+\gamma_-^2\right)^{1/3}$

d) $Ca(NO_3)_2$ $\gamma_\pm = \left(\gamma_+\gamma_-^2\right)^{1/3}$:

22. P4.13)

You want to make a pH 7.0 buffer using NaOH and phosphoric acid. The sum of the concentrations of all phosphoric acid species is 0.100 M. The equilibrium constants for concentrations given in mol L^{-1} for the following equilibria are

$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$ $(K_1 = 7.1 \times 10^{-3})$

$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$ $(K_2 = 6.2 \times 10^{-8})$

$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$ $(K_3 = 4.5 \times 10^{-13})$

(a) Write the equation that specifies that the solution is electrically neutral.

(b) Calculate the concentrations of all species in the buffer.

(c) Use data in table 4.2 to calculate K_2 at 37°C.

a) $[Na^+] + [H^+] = [OH^-] + [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}]$

b) $[HPO_4^{2-}]/[H_2PO_4^-] = K_2/[H^+] = (6.2 \times 10^{-8})/(10^{-7}) = 0.62$

Now $[H_3PO_4]$ and $[PO_4^{3-}] \ll [HPO_4^{2-}]$ or $[H_2PO_4^-]$ at pH 7

therefore $[HPO_4^{2-}] + [H_2PO_4^-] \approx 0.100M = 0.62[H_2PO_4^-] + [H_2PO_4^-]$

$[H_2PO_4^-] = 0.100\,M/1.62 = \underline{0.0617M}$

$[HPO_4^{2-}] = 0.62[H_2PO_4^-] = \underline{0.0383\,M}$

$[H_3PO_4] = (10^{-7}[H_2PO_4^-])/(7.1 \times 10^{-3}) = \underline{8.7 \times 10^{-7}M}$

$[PO_4^{3-}] = [HPO_4^{2-}]K_3/[H^+]$

$= (0.0383)(4.5 \times 10^{-13})/(10^{-7}) = \underline{1.72 \times 10^{-7}M}$

$[Na^+] = [H_2PO_4^-] + 2[HPO_4^{2-}] = \underline{0.1383\,M}$ from charge balance

c) $\ln K_2 = \ln K_1 - \Delta H^\circ (T_2^{-1} - T_1^{-1})/R$ (Table 4.2)

$= -16.60 - (4,150)(-1.299 \times 10^{-4})/8.314 = -16.54$

$K_2(310K) = \underline{6.58 \times 10^{-8}}$:

23. P5.11)

(a) Assume that Raoult's law holds and calculate the boiling point of a 2-M solution of urea in water.

(b) Urea actually forms complexes in solution in which two or more molecules hydrogen bond to form dimers and polymers. Will this effect tend to raise or lower the boiling point?

a) $\Delta T_b = K_b m = (0.51)(2) = 1.02$ (Eq. 5.52)

$T_b = \underline{101.02°C}$

b) Complex formation will lower the effective concentration of solute particles and lower the boiling point.

24. P5.24)

A protein solution containing 0.6 g of protein per 100 mL of solution has an osmotic pressure of 22 mm of water at 25°C and at a pH where the protein has no net charge (the isoelectric point). What is the molecular weight of the protein?

$M = wRT/\pi$

$w = 6.0\ g\ l^{-1}; \pi = (22\ \text{mm of } H_2O)\left(\dfrac{1\ \text{mm Hg}}{13.65\ \text{mm } H_2O}\right)\left(\dfrac{1\ \text{atm}}{760\ \text{mm Hg}}\right)$

$\pi = 2.12 \times 10^{-3}$ atm

$M = \dfrac{(6.0)(0.08205)(298)}{2.12 \times 10^{-3}}$

$M = \underline{69200}$

25. P5.31)

A 1.0 M sucrose solution and a 0.5 M sucrose solution next to each other in a sealed container at constant (both in water) in separate open vessels are placed temperature. What, if anything, will occur? Explain your answer briefly.

$$\ln(P_2 / P_1) = \frac{-\Delta \overline{H}_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$P_2 = 0.84 \text{ atm.}$$

26. P5.33)

The following device is a candidate for a perpetual motion machine:

Turbine blade

P_A

h

Solution

P_A^0

Pure solvent

Semipermeable membrane
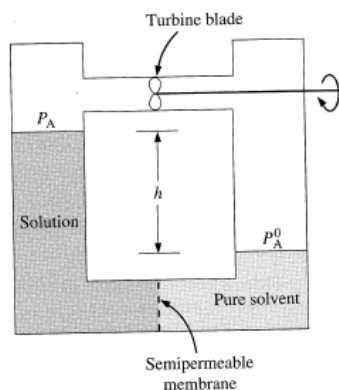
(1) All parts of the machine are at the *same* temperature T, equal to that of the heat bath surrounding the machine.

(2) The compartment at the left contains a solution, separated from the compartment at the right (containing pure solvent) by a semipermeable membrane, permitting solvent transfer only. A pressure difference $\Delta P = \rho g h$ balances the osmotic pressure difference Π across the membrane.

(3) The vapor pressure $P_A^{\bullet}$ above pure solvent is higher than the pressure P_A above the solution (Raoult's law). There is therefore a pressure difference $\Delta P = P_A^{\bullet} - P_A$ in the tube, and the flow of vapor in the upper connecting tube, from right to left, drives a turbine blade.

(4) Vapor moving through the connecting tube condenses at the surface of the solution. It tends to dilute

the solution, therefore reducing its osmotic pressure. This means that solvent will flow back through the semipermeable membrane, restoring the original concentration of the solution.

(5) The solvent is therefore set into perpetual motion, flowing as vapor from right to left in the upper

part and from left to right in the lower part, yielding energy.

Analyze the operation of this machine carefully. First, decide whether this machine works or fails. Then defend your answer as quantitatively and clearly as possible.

The machine fails. It violates the second law by obtaining work at constant temperature in a cyclic process. The reason the machine does not work, however, is that gravity affects the distribution of gas molecules in the container. The vapor pressure is highest at the interface of the gas and liquid and decreases with increasing height.

The height difference between the two sides is h. On the pure solvent side, the barometric equation describes the fractional vapor pressure (at height h (P) vs. at the interface (P_o)):

$P = P_o \exp(-mgh/RT)$ where $m = .018$ kg mol^{-1} and $g = 9.8$ m s^{-2}

$\frac{P_o}{P} = \exp(-mgh/RT)$

On the solution side of the membrane, the fractional vapor pressure (of the solution (P) vs. the pure solvent (P_o)) is related to the osmotic pressure by the following equations:

(1) $a_A = \dfrac{P_o}{P}$ (2) $\ln a_A = \dfrac{-\pi \overline{V}_A}{RT}$ so $\dfrac{P_o}{P} = \exp(-\pi \overline{V}_A / RT)$

From the book we know that $\pi = \rho g h$ and $\pi \overline{V}_A = \rho g h \overline{V}_A$

$\rho \times \overline{V}_A = m$ (molar mass of water)

so $\dfrac{P_o}{P} = \exp(-mgh/RT)$

Notice that the expressions for the fractional pressure on each side are identical. Thus at height h, there is no pressure differential, and thus no vapor flow.

Atkins Ch. 6 Exercises:

<u>27.</u> P6.5 (b)

(b) Molecular bromine is 24 per cent dissociated at 1600 K and 1.00 bar in the equilibrium $Br_2(g) \rightleftharpoons 2\,Br(g)$. Calculate K at (a) 1600 K, (b) 2000 K given that $\Delta_r H^\circ = +112$ kJ mol^{-1} over the temperature range.

6.6(a) From :

(a) $Br_2(g) \rightleftharpoons 2\,Br(g)$ $T = 1600$ K, $p = 1$ bar $= p^\circ$, $\alpha = 0.24$ at equilibrium.

We draw up the following equilibrium table (Example 6.2):

	$Br_2(g)$	$Br(g)$
Amount at equilibrium	$(1-\alpha)n$	$2\alpha n$
Mole fraction	$\dfrac{1-\alpha}{1+\alpha}$	$\dfrac{2\alpha}{1+\alpha}$
Partial pressure	$\dfrac{(1-\alpha)p}{1+\alpha}$	$\dfrac{2\alpha p}{1+\alpha}$

$$K = \left(\prod_J a_J^{\nu_J}\right)_{\text{equilibrium}} \quad [6.13] = \left(\prod_J (p_J/p^\circ)^{\nu_J}\right)_{\text{equilibrium}} \quad \text{[perfect gas assumption]}$$

$$= \frac{(p_{Br}/p^\circ)^2}{p_{Br_2}/p^\circ} = \frac{p_{Br}^2}{p_{Br_2}p^\circ} = \frac{\left(\dfrac{2\alpha p}{1+\alpha}\right)^2}{\left(\dfrac{(1-\alpha)p}{1+\alpha}\right)p^\circ}$$

$$= \frac{4p}{p^\circ}\left\{\frac{\alpha^2}{(1-\alpha)\times(1+\alpha)}\right\} = 4\left\{\frac{(0.24)^2}{(1-0.24)\times(1+0.24)}\right\}$$

$$= \boxed{0.24\overline{4}} \text{ at } 1600 \text{ K}$$

(b) $\ln K_2 = \ln K_1 - \dfrac{\Delta_r H^\circ}{R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$ [6.23]

$$\ln K_{2000\,K} = \ln K_{1600\,K} - \frac{\Delta_r H^\circ}{R}\left(\frac{1}{2000\text{ K}} - \frac{1}{1600\text{ K}}\right)$$

$$= \ln(0.24\overline{4}) - \left(\frac{+112\times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1}\text{mol}^{-1}}\right)\times\left(\frac{1}{2000\text{ K}} - \frac{1}{1600\text{ K}}\right) = 027\overline{3}$$

$$K_{2000\,K} = e^{0.27\overline{3}} = \boxed{1.3}$$

As expected, the temperature increase causes a shift to the right when the reaction is endothermic.

(b) Molecular bromine is 24 per cent dissociated at 1600 K and 1.00 bar in the equilibrium $Br_2(g) \rightleftharpoons 2\ Br(g)$. Calculate K at (a) 1600 K, (b) 2000 K given that $\Delta_r H^\circ = +112$ kJ mol^{-1} over the temperature range.

6.6(a) From :

$$CH_4(g) + 3\ Cl_2(g) \rightleftharpoons CHCl_3(l) + 3\ HCl(g)$$
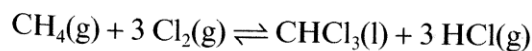
(a)   Using data tables at 25°C, we find

$$\Delta_r G^\circ = \Delta_f G^\circ(CHCl_3,l) + 3\ \Delta_f G^\circ(HCl,g) - \Delta_f G^\circ(CH_4,g)$$
$$= (-73.66\ KJ\ mol^{-1}) + (3) \times (-95.30\ KJ\ mol^{-1}) - (-50.72\ KJ\ mol^{-1})$$
$$= \boxed{-308.84\ kJ\ mol^{-1}}$$

$$\Delta_r H^\circ = \Delta_f H^\circ(CHCl_3,l) + 3\ \Delta_f H^\circ(HCl,g) - \Delta_f H^\circ(CH_4,g)$$
$$= (-134.47\ kJ\ mol^{-1}) + (3) \times (-92.31\ kJ\ mol^{-1}) - (-74.81\ kJ\ mol^{-1})$$
$$= -336.59\ kJ\ mol^{-1}$$

$$\ln K = \frac{-\Delta_r G^\circ}{RT}\ [6.14] = \frac{-(-308.84 \times 10^3\ J\ mol^{-1})}{(8.3145\ J\ K^{-1}\ mol^{-1}) \times (298.15\ K)} = 124.6$$

$$K = e^{124.6} = \boxed{1.30 \times 10^{54}}$$

(b) $$\ln K_2 = \ln K_1 - \frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\ [6.23]$$

$$\ln K_{50°C} = \ln K_{25°C} - \frac{\Delta_r H^\circ}{R}\left(\frac{1}{323.15\ K} - \frac{1}{298.15\ K}\right)$$

$$= \ln(1.30 \times 10^{54}) - \left(\frac{-336.59 \times 10^3\ J\ mol^{-1}}{8.3145\ J\ K^{-1}\ mol^{-1}}\right) \times \left(\frac{1}{323.15\ K} - \frac{1}{298.15\ K}\right) = 114.\overline{1}$$

$$K_{50°C} = e^{114.\overline{1}} = \boxed{3.57 \times 10^{49}}$$

As expected, the temperature increase causes a shift to the left when the reaction is exothermic.

$$\Delta_r G^\circ = -RT\ln K\ [6.14]$$

$$\Delta_r G^\circ_{50°C} = -(8.3145\ J\ K^{-1}\ mol^{-1}) \times (323.15\ K)\ln(3.75 \times 10^{49}) = \boxed{-307\ kJ\ mol^{-1}}$$

tion $\Delta\nu = \sum \nu_I = -2$

29. P6.10(b)

6.10(b) The equilibrium constant of a reaction is found to fit the expression $\ln K = A + B/T + C/T^3$ between 400 K and 500 K with $A = -2.04$, $B = -1176$ K, and $C = 2.1 \times 10^7$ K^3. Calculate the standard reaction enthalpy and standard reaction entropy at 450 K.
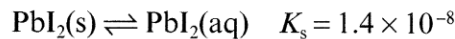
$$\ln K = A + \frac{B}{T} + \frac{C}{T^3}, \quad \text{where} \quad A = -2.04,\ B = -1176\ \text{K, and}\ C = 2.1 \times 10^7\ \text{K}^3$$

At 450 K:

$$\Delta_r G^\circ = -RT \ln K\ [6.14] = RT \times \left(A + \frac{B}{T} + \frac{C}{T^3} \right)$$

$$= -(8.3145\ \text{J K}^{-1}\text{mol}^{-1}) \times (450\ \text{K}) \times \left(-2.04 - \frac{1176\ \text{K}}{450\ \text{K}} + \frac{2.1 \times 10^7\ \text{K}^3}{(450\ \text{K})^3} \right) = +16.6\ \text{kJ mol}^{-1}$$

30. P6.19 (b)

6.19(b) For $PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\ I^-(aq)$, $K = 1.4 \times 10^{-8}$ at 25°C and the standard Gibbs energy of formation of $PbI_2(s)$ is -173.64 kJ mol^{-1}. Calculate the standard Gibbs energy of formation of $PbI_2(aq)$.

$$PbI_2(s) \rightleftharpoons PbI_2(aq) \quad K_s = 1.4 \times 10^{-8}$$

$$\Delta_r G^\circ = -RT \ln K_s$$
$$= -(8.3145\ \text{J K}^{-1}\text{mol}^{-1}) \times (298.15\ \text{K}) \times \ln(1.4 \times 10^{-8}) = +44.8\ \text{kJ mol}^{-1}$$
$$= \Delta_f G^\circ(PbI_2,aq) - \Delta_f G^\circ(PbI_2,s)$$

$$\Delta_f G^\circ(PbI_2,aq) = \Delta_r G^\circ + \Delta_f G^\circ(PbI_2,s)$$
$$= (44.8 - 173.64)\ \text{kJ mol}^{-1} = \boxed{-128.8\ \text{kJ mol}^{-1}}$$

P.S. How to derive the equation used in part a and c of Prob.1.

Set choloro=A, bromo=B, and for an ideal solution of A plus B, we have: $p_A = py_A;\ p_B = py_B$

$$p_A = p_A^* x_A;\ p_B = p_B^* x_B$$
$$p = p_A + p_B = p_A^* x_A + p_B^* x_B$$
$$x_A = 1 - x_B$$
$$\Rightarrow \boxed{p = p_A^* + \left(p_B^* - p_A^* \right)x_B}$$

Therefore,

$$y_A = \frac{p_A}{p} = \frac{p_A^* x_A}{p} = \frac{p_A^* x_A (p_A^* - p_B^*)}{p(p_A^* - p_B^*)} \qquad \text{Multiply the same term}$$

$$\Rightarrow y_A = \frac{p_A^*(1 - x_B)(p_A^* - p_B^*)}{p(p_A^* - p_B^*)} \qquad \text{Because} \quad x_A = 1 - x_B$$

$$\Rightarrow y_A = \frac{p_A^*(p_A^* - p_B^* - x_B p_A^* + x_B p_B^*)}{p(p_A^* - p_B^*)} \qquad \begin{array}{l}\text{Substitute the}\\ \text{highlighted equation in}\end{array}$$

$$\Rightarrow y_A = \frac{p_A^*(p - p_B^*)}{p(p_A^* - p_B^*)} \qquad \text{Done proof}$$