1. Cyclohexane can be cracked to form benzene and hydrogen gas by the following reaction:

$C_6H_{12}(g) \rightarrow C_6H_6(g) + 3\,H_2(g)$ $\Delta H^\circ = +206.1\ \text{kJ mol}^{-1}$

$\Delta S^\circ = +363.0\ \text{J K}^{-1}\ \text{mol}^{-1}$

a. (6 pts) Calculate ΔG° for the reaction.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= 206100\ \text{J/mol} - 298\text{K}\,(363.0\ \text{J/mol K})$$

$$\boxed{\Delta G^\circ = +97926\ \text{J/mol}}$$

b. (7 pts) Will there be a reaction if C_6H_6, C_6H_{12}, and H_2, each 1 atm partial pressure, are mixed at room temperature? In which direction?

$$\Delta G = \Delta G^\circ + RT \ln \underbrace{\frac{P(H_2)^3\,P(C_6H_6)}{P(C_6H_{12})}}_{1}$$

$$\Delta G = \Delta G^\circ = +97926\ \text{J/mol}$$

$$\boxed{\text{Reaction occurs to the left (toward reactants)}}$$

c. (7pts) At what temperature would the mixture described in part b be at equilibrium?

equilibrium $\Delta G = \Delta G^\circ = 0$

assume ΔH°, ΔS° indep. of temp

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{201.6\ \text{kJ/mol}}{0.363\ \text{kJ/mol K}}$$

$$\boxed{T = 568\ \text{K}}$$

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3. Consider the following process: $COCl_2(g) \leftrightarrow CO(g) + Cl_2(g)$
Equilibrium constant, K, is measured at two different temperatures:

K(635.7 K) = 0.01950
K(760.2 K) = 0.5183

Assume ideal gas behavior and take ΔH° to be independent of temperature.

a. (6pts) What is ΔH°?

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^\circ}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$\ln \frac{0.5183}{0.01950} = -\frac{\Delta H^\circ}{8.314\ \text{J/mol K}}\left[\frac{1}{760.2\ \text{K}} - \frac{1}{635.7\text{K}}\right]$$

$$\boxed{\Delta H^\circ = +105855\ \text{J/mol}}$$

b. (6pts) What value do you expect for the equilibrium constant, K, at T = 500 Kelvin?

$$\ln \frac{K_{500}}{0.5183} = \frac{-105855\ \text{J/mol}}{8.314\ \text{J/mol K}}\left[\frac{1}{500\ \text{K}} - \frac{1}{760.2\ \text{K}}\right]$$

$$\boxed{K_{500} = 8.498 \times 10^{-5}}$$

c. (6pts) What is ΔG° at T = 500 K?

$$\Delta G^\circ = -RT \ln K_{500}$$

$$= -8.314\ \text{J/mol K}\ (500\text{K}) \ln 8.498 \times 10^{-5}$$

$$\boxed{\Delta G^\circ = +38964\ \text{J/mol}}$$

4. A single stranded oligonucleotide that has complementary ends can form a base-paired loop. For the oligonucleotide $A_5C_6U_5$:

$$\text{AAAAACCCCCCUUUUU} \xleftrightarrow{K_1} \begin{array}{lc} & \text{CC} \\ \text{AAAAA} & \text{C} \\ \text{UUUUU} & \text{C} \\ & \text{CC} \end{array}$$

a. (10 pts) At 25°C, the equilibrium constant $K_1 = 0.53$. What are the concentrations of the loop, [Loop], and single strand, [SS], if you begin with 1.0 mM single strand?

$$K_1 = 0.53 = \frac{[\text{LOOP}]}{[\text{SS}]} = \frac{x}{10^{-3} - x}$$

$$5.3 \times 10^{-4} - 0.53x = x \Rightarrow \frac{5.3 \times 10^{-4}}{1.53} = \frac{1.\cancel{53}\,x}{1.\cancel{53}}$$

$$[x] = [\text{LOOP}] = 3.46 \times 10^{-4}\ \text{M} = \boxed{0.346\ \text{mM}}$$

$$[\text{SS}] = 10^{-3} - x = 6.54 \times 10^{-4}\ \text{M} = \boxed{0.654\ \text{mM}}$$

b. (10 pts) At higher concentrations of oligonucleotide, another reaction becomes possible. A double stranded molecule with an internal loop can form, [DS].

$$2\ A_5C_6U_5 \xleftrightarrow{K_2} \begin{array}{ccc} & C_6 & \\ A_5 & & U_5 \\ U_5 & & A_5 \\ & C_6 & \end{array}$$

At 25 °C, $K_2 = 0.86 \times 10^{-2}\ M^{-1}$.

Calculate the concentrations of all three species: [SS], [Loop], [DS] at equilibrium when you begin with a solution containing an initial concentration of [SS] = 0.1 M.

mass conserve

$$[\text{SS}] + [\text{LOOP}] + 2[\text{DS}] = 0.100\text{M}$$

$$K_2 = \frac{[\text{DS}]}{[\text{SS}]^2} = 0.86 \times 10^{-2} \Rightarrow [\text{DS}] = [\text{SS}]^2 K_2$$

$$K_1 = \frac{[\text{LOOP}]}{[\text{SS}]} = 0.53 \Rightarrow [\text{LOOP}] = [\text{SS}]\underset{K_1}{\underset{\uparrow}{0.53}}$$

$$[\text{SS}] + 0.53[\text{SS}] + 2(0.86 \times 10^{-2})[\text{SS}]^2 = 0.100$$

$$0.0172[\text{SS}]^2 + 1.53[\text{SS}] - 0.100 = 0$$

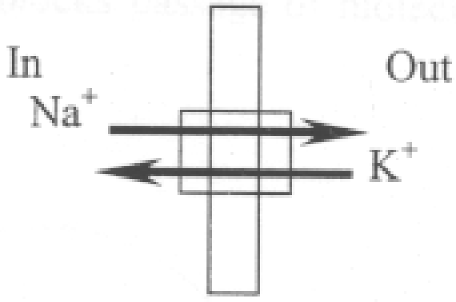
use quadratic equation to solve for $[\text{SS}] = x$

$$[\text{SS}] = 6.53 \times 10^{-2}\ \text{M},\ [\text{DS}] = 3.667 \times 10^{-5}\ \text{M},$$

$$[\text{LOOP}] = 3.461 \times 10^{-2}\ \text{M}$$

5. Active transport in cells drives substances from regions of low chemical potential to regions of high chemical potential. The *sodium-potassium* ion pump in the cell membrane is an example of an active transporter. It drives Na^+ out and K^+ in with the following stoichiometry:

$$3Na^+(in) + 2K^+(out) \rightarrow 3Na^+(out) + 2K^+(in)$$



a. (7 pts) What is the sign of the free energy change of the *sodium-potassium* system assuming you begin at equilibrated concentrations of Na^+ and K^+?

active transport has $\Delta G > 0$ because it is not a spontaneous process

$$\boxed{\Delta G > 0\text{, positive}}$$

b. (7 pts) Write an expression for ΔG of this process.

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$\boxed{\Delta G = \Delta G^\circ + RT \ln \left[\frac{[Na^+(out)]^3\,[K^+(in)]^2}{[Na^+(in)]^3\,[K^+(out)]^2}\right]}$$

c. (6 pts) Suppose another, unrelated process, reduces $[Na^+]$ outside of the cell by a factor of 2. How does this change ΔG? (Be as quantitative as you can.)

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{\left[\frac{Na^+(out)}{2}\right]^3\,[K^+(in)]^2}{[Na^+(in)]^3\,[K^+(out)]^2}\right)$$

Before... $\Delta G = \Delta G^\circ + RT \ln X$

After... $\Delta G = \Delta G^\circ + RT \ln \left[\left(\tfrac{1}{2}\right)^3 X\right]$

$= \Delta G^\circ + RT \ln \left[\tfrac{1}{8} X\right]$

ΔG decreases (more negative) by a factor of $\ln\left(\frac{1}{8}\right)$!

a. (2pts) What is the equilibrium state for this system?

$$P_A^l = P_A^r$$

$$P_B^r + P_A^r = P$$

$$P_A^l = P$$

Initial State

A B

n_A n_B

Equilibrium State

A B

— n_A, n_B

b. (3 pts) Write an expression for the free energy change from the initial state to the equilibrium configuration.

$$\Delta G_{mix} = n_A RT \ln X_A + n_B RT \ln X_B$$

c. (5 pts) What is the equilibrium state of the system if the left balloon is rigid instead of flexible?

$$P_A^l = P_A^r$$

$$\frac{n_A^l RT}{V^l} = \frac{n_A^r RT}{V^r}$$

$$V^l = \frac{n_A RT}{P}$$

$$V^r = \frac{(n_A^r + n_B) RT}{P}$$

$$\frac{n_A^l}{n_A} = \frac{n_A^r}{n_A^r + n_B}$$

$$n_A^l = n_A - n_A^r$$

$$\frac{n_A - n_A^r}{n_A} = \frac{n_A^r}{n_A^r + n_B}$$

$$1 - \frac{n_A^r}{n_A} = \frac{n_A^r}{n_A^r + n_B}$$

$$\cancel{n_A^r} + n_B - \frac{n_A^r(n_A^r + n_B)}{n_A} = \cancel{n_A^r}$$

$$n_A^r(n_A^r + n_B) - n_A n_B = 0$$

$$(n_A^r)^2 + n_B(n_A^r) - n_A n_B = 0$$

Use quadratic formula

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$n_A^r = \frac{-n_B \pm \sqrt{n_B^2 - 4 n_A n_B}}{2}$$

n_B is positive, so must use ⊕ root

$$\boxed{n_A^r = -\frac{n_B}{2} + \sqrt{\left(\frac{n_B}{2}\right)^2 + n_A n_B}}$$