Chem 338

Homework Set #7 solutions October 24, 2001

From Atkins: 7.2, 7.3, 7.6, 7.7, 7.9, 7.16, 7.23, 7.34, 7.39

7.2) The concentration of fructose 6-phosphate (F6P) and fructose 1,6-biphosphate (F16bP), ATP, and ADP in muscle tissue were measured as 0.089, 0.012, 12.0, and 1.2 mmol/L. For the reaction F6P(aq) + ATP(aq) → F16bP(aq) + ADP(aq) at 37ºC, the standard Gibbs energy (at pH=7) is –18.3 kJ/mol. (a) Calculate the reaction quotient and the reaction Gibbs energy for the reaction in the muscle tissue environment. (b) Is the reaction spontaneous?

a) For the reaction as written,

$$Q = \frac{[\mathrm{F16bP}][\mathrm{ADP}]}{[\mathrm{F6P}][\mathrm{ATP}]} = \frac{(0.012)(1.2)}{(0.089)(12.0)} = 0.01348 \cong 0.013$$

$$\begin{aligned} \Delta G_r &= \Delta G_r^o + RT\ln Q \\ &= -18.3 + (8.31451\times 10^{-3})(310)\ln(0.01348) \\ &= -29.4\ \mathrm{kJ/mol} \end{aligned}$$

b) Yes, it is spontaneous since $\Delta G_r < 0$

7.3) The standard Gibbs energy of formation of $NH_3(g)$ is –16.5 kJ/mol at 298 K. What is the reaction Gibbs energy when the partial pressures of the N_2, H_2, and NH_3 (treated as perfect gases) are 3.0 bar, 1.0 bar, and 4.0 bar, respectively? What is the spontaneous direction of the reaction in this case?

The formation reaction is (per mole NH_3): $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow NH_3$ and $\Delta G_f^o = \Delta G_r^o$

$$\begin{aligned} \Delta G_r &= \Delta G_r^o + RT\ln\frac{p_{NH_3}}{\left(p_{N_2}\right)^{1/2}\left(p_{H_2}\right)^{3/2}} \\ &= -16.5 + (298)(8.31451\times 10^{-3})\ln\frac{4.0}{(3.0)^{1/2}(1.0)^{3/2}} \\ &= -14.4\ \mathrm{kJ/mol} \end{aligned}$$

The spontaneous direction is towards products.

7.6) The equilibrium constant for the reaction A + B $\rightleftarrows$ 2C is reported as 3.4 x 10^4.

What would it be for the reaction written as

(a) 2A + 2B $\rightleftarrows$ 4C, (b) $\frac{1}{2}$A + $\frac{1}{2}$B $\rightleftarrows$ C

For the original reaction, $K = \dfrac{[\mathrm{C}]^2}{[\mathrm{A}][\mathrm{B}]}$, and multiplying the reaction by a constant raises the equilibrium constant by that power:

(a) $K' = \dfrac{[\mathrm{C}]^4}{[\mathrm{A}]^2[\mathrm{B}]^2} = (K)^2 = 1.2\times 10^9$

(b) $\sqrt{K}$ = 1.8 x 10^2

7.7) The equilibrium constant for the isomerization of *cis*-2-butene to *trans*-2-butene is *K*=2.07 at 400 K. Calculate the standard reaction Gibbs energy for the isomerization.

$$\Delta G_r^o = -RT\ln K = -(8.31451)(400)\ln(2.07) = 2.42\times 10^3 \text{ J/mol}$$
$$= \text{-2.42 kJ/mol}$$

7.9) One biochemical reaction has a standard Gibbs energy of –200 kJ/mol and a second biochemical reaction has a standard Gibbs energy of –100 kJ/mol. What is the ratio of their equilibrium constants at 310 K?

For each reaction, $\Delta G_r^o = -RT\ln K$:

$$\frac{-100}{-200} = \frac{\ln K_2}{\ln K_1}$$

$$\frac{1}{2} = \frac{\ln K_2}{\ln K_1}$$

$$\tfrac{1}{2}\ln K_1 = \ln K_2$$

$$\ln K_1^{1/2} = \ln K_2$$

$$K_2 = K_1^{1/2}$$

7.16) Use the information in Appendix 1 to estimate the temperature at which (a) $CaCO_3$ decomposes spontaneously and (b) $CuSO_4 \bullet 5H_2O$ undergoes dehydration.

Using the relation $\Delta G^o = \Delta H^o - T\Delta S^o$, the breakeven point in the spontaneity of a process is when $\Delta G^o = 0$. If we assume ΔH^o and ΔS^o are independent of temperature, the temperature at which this occurs is obtained from $T = \dfrac{\Delta H^o}{\Delta S^o}$. In the following the ΔH_r^o's are obtained from ΔH_f^o data and the ΔS_r^o are obtained from standard molar entropies, S_m^o.

a) for $CaCO_3 \rightarrow CaO + O_2$

$$\Delta H_r^o = -635.1 + (-393.5) - (-1206.9) = 178.3 \text{ kJ/mol}$$

$$\Delta S_r^o = 39.75 + 213.74 - 92.9 = 160.6 \text{ J K}^{-1}\text{ mol}^{-1}$$

$$T = \frac{178.3\times10^3}{160.6} = 1110 \text{ K}$$

b) for $CuSO_4 \cdot 5H_2O(s) \rightarrow CuSO_4(s) + 5H_2O(g)$

$$\Delta H_r^o = (-771.36) + 5(-241.82) - (-2279.7) = 299.24 \text{ kJ/mol}$$

$$\Delta S_r^o = (109) + 5(188.83) - (300.4) = 752.75 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$T = \frac{299.24 \times 10^3}{752.75} = 398 \text{ K}$$

7.23) Could the synthesis of ammonia be used as the basis of a fuel cell? What is the maximum electrical energy output for the consumption of 100 g of nitrogen?

The synthesis of ammonia could be used as a fuel cell since it is a spontaneous reaction. Remembering that the maximum amount of non-expansion work (e.g., electrical work) is given by ΔG, for 100 g of N_2:

For the reaction, $N_2 + 3H_2 \rightarrow 2NH_3$,

$$\Delta G_r = 2(-16.45) - (0) - 3(0) \quad = -32.9 \text{ kJ/mol} \qquad (\text{using } \Delta G_f\text{'s})$$

$$100 \text{ g } N_2 \times \frac{1 \text{ mol}}{28.013 \text{ g}} = 3.570 \text{ mol}$$

$$3.570 \text{ mol } N_2 \times 32.9 \ \frac{\text{kJ}}{\text{mol } N_2} = 117.4 \text{ kJ}$$

7.34) The equilibrium constant of the reaction $2C_3H_6(g) \rightleftarrows C_2H_4(g) + C_4H_8(g)$ is found to fit the expression (T in kelvin)

$$\ln K = -1.04 - \frac{1088}{T} + \frac{1.51 \times 10^5}{T^2}$$

between 300 K and 600 K. Calculate the standard reaction enthalpy and standard reaction entropy at 400 K. (Hint: Begin by calculating ln *K* at 390 K and 410 K; then use eqn. 7.14.)

$$\text{At 390 K, } \ln K = -1.04 - \frac{1088}{390} + \frac{1.51 \times 10^5}{390^2} = -2.83698$$

At 410 K, $\ln K' = -1.04 - \dfrac{1088}{410} + \dfrac{1.51\times10^5}{410^2} = -2.79538$

the van't Hoff equation yields: $\ln K' - \ln K = \dfrac{\Delta H_r^o}{R}\left(\dfrac{1}{390} - \dfrac{1}{410}\right)$

re-arranging for the enthalpy and substituting,

$$\Delta H_r^o = \frac{R(-2.79538 + 2.83698)}{\left(\frac{1}{390} - \frac{1}{410}\right)} = 2.765 \text{ kJ/mol}$$

At 400 K, the equation above for the T dependence of ln K yields ln $K = -2.81625$

and $\Delta G_r^o = -RT\ln K = -(8.31451\times10^{-3})(400)(-2.81625) = 9.37 \text{ kJ/mol}$

Finally, $\Delta S_r^o = \dfrac{\Delta H_r^o - \Delta G_r^o}{T} = -16.5 \text{ J K}^{-1} \text{ mol}^{-1}$

7.39) In a gas-phase equilibrium mixture of $SbCl_5$, $SbCl_3$, and Cl_2 at 500 K, $p_{SbCl_5} = 0.15$ bar, $p_{SbCl_3} = 0.20$ bar. Calculate the equilibrium partial pressure of Cl_2 given that K=3.5 x 10^{-4} for the reaction $SbCl_5(g) \rightleftarrows SbCl_3(g) + Cl_2(g)$.

$$K = \frac{p_{SbCl_3}p_{Cl_2}}{p_{SbCl_5}} = 3.5\times10^{-4}$$

$$= \frac{(0.20)p_{Cl_2}}{0.15}$$

$$p_{Cl_2} = 2.6\times10^{-4} \text{ bar}$$