

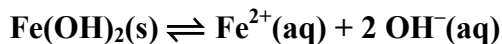
23 Calculate K_p for the following reaction at 25°C:



Find the value of K by solving Equation (18.14) of the text.

$$K_p = e^{\frac{-\Delta G^\circ}{RT}} = e^{\frac{-2.60 \times 10^3 \text{ J/mol}}{(8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K})}} = e^{-1.05} = 0.35$$

25 Consider the following reaction at 25°C:



Calculate ΔG° for the reaction. K_{sp} for $\text{Fe}(\text{OH})_2$ is 1.6×10^{-14} .

$$K_{sp} = [\text{Fe}^{2+}][\text{OH}^-]^2 = 1.6 \times 10^{-14}$$

$$\Delta G^\circ = -RT \ln K_{sp} = -(8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K}) \ln(1.6 \times 10^{-14}) = 7.9 \times 10^4 \text{ J/mol} = 79 \text{ kJ/mol}$$

27 (a) Calculate ΔG° and K_p for the following equilibrium reaction at 25°C. The ΔG_f° values are 0 for $\text{Cl}_2(\text{g})$, -286 kJ/mol for $\text{PCl}_3(\text{g})$, and -325 kJ/mol for $\text{PCl}_5(\text{g})$.

We first find the standard free energy change of the reaction.

$$\begin{aligned} \Delta G_{\text{rxn}}^\circ &= \Delta G_f^\circ[\text{PCl}_3(\text{g})] + \Delta G_f^\circ[\text{Cl}_2(\text{g})] - \Delta G_f^\circ[\text{PCl}_5(\text{g})] \\ &= (1)(-286 \text{ kJ/mol}) + (1)(0) - (1)(-325 \text{ kJ/mol}) = 39 \text{ kJ/mol} \end{aligned}$$

We can calculate K_p using Equation (18.14) of the text.

$$K_p = e^{\frac{-\Delta G^\circ}{RT}} = e^{\frac{-39 \times 10^3 \text{ J/mol}}{(8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K})}} = e^{-16} = 1 \times 10^{-7}$$

(b) Calculate ΔG for the reaction if the partial pressures of the initial mixture are $P_{\text{PCl}_5} = 0.0029$ atm, $P_{\text{PCl}_3} = 0.27$ atm, and $P_{\text{Cl}_2} = 0.40$ atm.

We are finding the free energy difference between the reactants and the products at their nonequilibrium values. The result tells us the direction of and the potential for further chemical change. We use the given nonequilibrium pressures to compute Q_p .

$$Q_p = \frac{P_{\text{PCl}_3} P_{\text{Cl}_2}}{P_{\text{PCl}_5}} = \frac{(0.27)(0.40)}{0.0029} = 37$$

The value of ΔG (notice that this is not the standard free energy difference) can be found using Equation (18.13) of the text and the result from part (a).

$$\Delta G = \Delta G^\circ + RT \ln Q = (39 \times 10^3 \text{ J/mol}) + (8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K}) \ln(37) = 48 \text{ kJ/mol}$$

Which way is the direction of spontaneous change for this system? What would be the value of ΔG if the given data were equilibrium pressures? What would be the value of Q_p in that case?

29 Consider the decomposition of calcium carbonate:

Calculate the pressure in atm of CO_2 in an equilibrium process (a) at 25°C and (b) at 800°C . Assume that $\Delta H^\circ = 177.8 \text{ kJ/mol}$ and $\Delta S^\circ = 160.5 \text{ J/K}\cdot\text{mol}$ for the temperature range.

The expression of K_p is: $K_p = P_{\text{CO}_2}$

Thus you can predict the equilibrium pressure directly from the value of the equilibrium constant. The only task at hand is computing the values of K_p using Equations (18.10) and (18.14) of the text.

(a) At 25°C , $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = (177.8 \times 10^3 \text{ J/mol}) - (298 \text{ K})(160.5 \text{ J/K}\cdot\text{mol}) = 130.0 \times 10^3 \text{ J/mol}$

$$P_{\text{CO}_2} = K_p = e^{\frac{-\Delta G^\circ}{RT}} = e^{\frac{-130.0 \times 10^3 \text{ J/mol}}{(8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K})}} = e^{-52.47} = 1.6 \times 10^{-23} \text{ atm}$$

(b) At 800°C , $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = (177.8 \times 10^3 \text{ J/mol}) - (1073 \text{ K})(160.5 \text{ J/K}\cdot\text{mol}) = 5.58 \times 10^3 \text{ J/mol}$

$$P_{\text{CO}_2} = K_p = e^{\frac{-\Delta G^\circ}{RT}} = e^{\frac{-5.58 \times 10^3 \text{ J/mol}}{(8.314 \text{ J/K}\cdot\text{mol})(1073 \text{ K})}} = e^{-0.625} = 0.535 \text{ atm}$$

What assumptions are made in the second calculation?

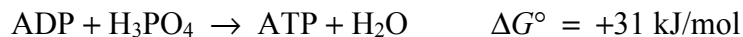
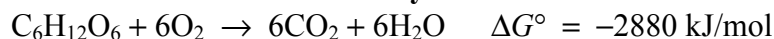
31 At 25°C , ΔG° for the process $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$ is 8.5 kJ/mol . Calculate the vapor pressure of water at this temperature.

The equilibrium constant expression is: $K_p = P_{\text{H}_2\text{O}}$

We are actually finding the equilibrium vapor pressure of water (compare to Problem 29). We use Equation (18.14) of the text.

$$P_{\text{H}_2\text{O}} = K_p = e^{\frac{-\Delta G^\circ}{RT}} = e^{\frac{-8.6 \times 10^3 \text{ J/mol}}{(8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K})}} = e^{-3.47} = 3.1 \times 10^{-2} \text{ atm}$$

The positive value of ΔG° implies that reactants are favored at equilibrium at 25°C . Is that what you would expect?

35 Referring to the metabolic process involving glucose on p. 787, calculate the maximum number of moles of ATP that can be synthesized from ADP from the breakdown of one mole of glucose.

Maximum number of ATP molecules synthesized:

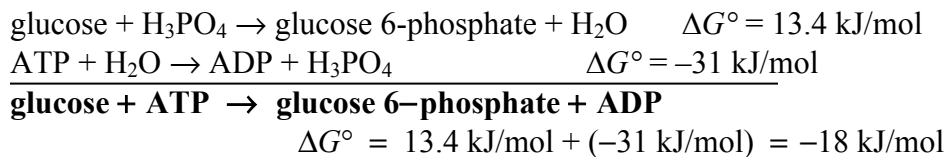
$$2880 \text{ kJ/mol} \times \frac{1 \text{ ATP molecule}}{31 \text{ kJ/mol}} = 93 \text{ mol ATP}$$

36 In the metabolism of glucose, the first step is the conversion of glucose to glucose 6-phosphate:



Because ΔG° is positive, this reaction does not favor the formation of products. Show how this reaction can be made to proceed by coupling it with the hydrolysis of ATP. Write an equation for the coupled reaction and estimate the equilibrium constant for the coupled process.

The equation for the coupled reaction is:



As an estimate:

$$\ln K = \frac{-\Delta G^\circ}{RT}$$

$$\ln K = \frac{-(-18 \times 10^3 \text{ J/mol})}{(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K})} = 7.3$$

$$K = e^{\frac{-(-18 \times 10^3 \text{ J/mol})}{(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K})}} = 1.4 \times 10^3$$