Problem 3.1
For reactions at constant pressure involving liquids and solids, it is commonly assumed that $\Delta H \approx \Delta E$. Why?

Purpose of problem
Test understanding of thermodynamic definitions and equations

Relevant section(s) of text
Sections 3.4.3 and 3.7

Solution
From eq. 3.2:

$dE = dH - PdV$ (at constant pressure), or:
$\Delta E = \Delta H - P\Delta V$

Since ΔV typically is very small for aqueous systems: $\boldsymbol{\Delta H \approx \Delta E}$

Problem 3.2

To illustrate the relationship in Problem 3.1, calculate ΔH and ΔE when 100 g of ice melts at $25^{\circ}C$ and 1 atm. How much heat is absorbed by the system? For ice: $\overline{H}^{o}_{f} = -292.80$ kJ/mol and molar volume = 0.0196 L/mol; for water: $\overline{H}^{o}_{f} = -285.83$ kJ/mol and molar volume = 0.0180 L/mol.

Purpose of problem

Test understanding of thermodynamic definitions and equations

Relevant section(s) of text

Sections 3.4.3 and 3.7

Solution

The reaction is: $H_2O(s) \rightarrow H_2O(l)$

We are interested in 100 g of ice = (100 g)/(18 g/mol) = 5.56 moles of ice

$\Delta H = \overline{H}^{o}_{f,water} - \overline{H}^{o}_{f,ice} = -285.83 - (-292.80) = 6.97$ kJ/mol or 38.75 kJ for 5.56 moles

$\Delta V = \Delta V_{water} - \Delta V_{ice} = 0.0180 - 0.0196 = -0.0016$ L/mol or -0.0089 L for 5.56 moles

From eq. 3.2:

$\Delta E = \Delta H - P\Delta V = 38.75$ kJ $- (1$ atm$)(-0.0089$ L$)(X$ kJ/L-atm$)$

where: X is the conversion factor from L-atm to kJ. From the ratio of the values of the ideal gas constant in Section 3.8.4, $R = 8.314 \times 10^{-3}$ kJ/mol-$^{\circ}$K and $R' = 0.082057$ L-atm/mol-$^{\circ}$K, $X = 0.1013$ kJ/L-atm.

So: $\Delta E = \Delta H - P\Delta V = 38.75$ kJ $- (1$ atm$)(-0.0089$ L$)(0.1013$ kJ/L-atm$) \approx$ **38.75 kJ**

Note that, as expected from Problem 3.1, the $P\Delta V$ term contributes little and $\Delta H \approx \Delta E$ for systems of condensed phases.

From eq. 3.3: $\Delta H = \Delta Q_P$

Thus: $\Delta Q_P = +38.75$ kJ and **38.75 kJ of heat is absorbed as the ice melts**

Problem 3.3
What pressure would be required to convert 1 g of graphite into 1 g of diamond at 25°C and 1 atm? Assume graphite and diamond are incompressible. The $\overline{G}_f^o$ values are 0 and –2.59 kJ/mol and densities are 2.25 and 3.51 g/cm³ for graphite and diamond, respectively. Hint: Start with eq. 3.8 and realize that temperature is constant here.

[Before you quit your day job to make 1 g (5 carat) diamonds, realize that artificial diamonds are made at much higher temperatures and pressures (> 100,000 atm) than you calculated. Graphite is dissolved in a molten metal catalyst and diamond precipitates. Why are the temperatures and pressures employed much higher than calculated here?]

Purpose of problem
Use of thermodynamic equations

Relevant section(s) of text
Section 3.5

Solution
Eq. 3.7 states: $dG = VdP - S_{sys}dT$
At constant temperature: $dG/dP = V$
Integrating for a chemical reaction: $\Delta G_{rxn} = P\Delta V_{rxn}$
    where: ΔV_{rxn} is the change in the molar volume during the reaction. The molar volume is the volume of one mole of material (equal to the molecular weight divided by the density)

The reaction is: C(graphite) $\rightarrow$ C(diamond)

We are interested in 1 g of graphite = (1 g)/(12 g/mol) = 0.0833 mole of graphite

    At 25°C: $\Delta G_{rxn} = \overline{G}_{f,graphite}^o - \overline{G}_{f,diamond}^o = -2.59 - 0 = -2.59$ kJ/mol or –0.22 kJ for 0.0833 mole

Also:

    ΔV_{rxn} = molar volume of diamond – molar volume of graphite
          = (12 g/mol)/(3510 g/L) – (12 g/mol)/(2250 g/L)
          = –1.91 L/mol or -1.59×10^{-4} L for 0.0833 mole

Thus:
    $\Delta G_{rxn} = P\Delta V_{rxn}$ or:
    P = $\Delta G_{rxn}/\Delta V_{rxn}$

$$= (-0.22 \text{ kJ})/(-1.59 \times 10^{-4} \text{ L}) = 1384 \text{ kJ/L}$$

From the ratio of the values of the ideal gas constant in Section 3.8.4, $R = 8.314 \times 10^{-3}$ kJ/mol-$^{\circ}$K and $R' = 0.082057$ L-atm/mol-$^{\circ}$K, 1 atm = 0.1013 kJ/L.

So: P (in atm) = (1384 kJ/L)/(0.1013 kJ/L-atm) = 13,660 atm

So graphite will equilibrate with the diamond phase at about 14,000 atm

In practice, higher temperatures and pressures are employed in the presence of a catalyst to make the reaction proceed more quickly.

Problem 3.4

Consider the reaction: $HSO_4^- \rightarrow SO_4^{2-} + H^+$. Is the reaction endothermic or exothermic if all concentrations are 1 M? Does the reaction proceed spontaneously as written if all concentrations are 1 M? For HSO_4^-: $\overline{H}_f^o = -887.3$ kJ/mol, $\overline{S}_f^o = 132$ J/mol-°K, and $\overline{G}_f^o = -756.0$ kJ/mol. For SO_4^{2-}: $\overline{H}_f^o = -909.2$ kJ/mol, $\overline{S}_f^o = 20.1$ J/mol-°K, and $\overline{G}_f^o = -744.6$ kJ/mol. For H^+: $\overline{H}_f^o = 0$ kJ/mol, $\overline{S}_f^o = 0$ J/mol-°K, and $\overline{G}_f^o = 0$ kJ/mol.

Purpose of problem

Use of thermodynamic equations

Relevant section(s) of text

Section 3.7

Solution

Since all concentrations are 1 M, you can use thermodynamic properties evaluated at standard state.

To determine if the reaction is endothermic or exothermic, calculate ΔH_{rxn}^o assuming all concentrations are 1 M:

$$\Delta H_{rxn}^o = \overline{H}_{f,SO_4^{2-}}^o - \overline{H}_{f,H^+}^o - \overline{H}_{f,HSO_4^-}^o = -909.2 + 0 - (-887.3) = -21.9 \text{ kJ/mol}$$

Heat is released ($\Delta Q_P = \Delta H_{rxn}^o < 0$) and therefore the reaction is exothermic if all concentrations are 1 M.

To determine if the reaction proceeds spontaneously, calculate ΔG_{rxn}^o assuming all concentrations are 1 M:

$$\Delta G_{rxn}^o = \overline{G}_{f,SO_4^{2-}}^o - \overline{G}_{f,H^+}^o - \overline{G}_{f,HSO_4^-}^o = -744.6 + 0 - (-756.0) = +11.4 \text{ kJ/mol}$$

$\Delta G_{rxn}^o > 0$ and therefore the reaction does not proceed spontaneously as written (assuming that all concentrations are 1 M).

Problem 3.5

Consider the reaction: $NH_4^+ \rightarrow NH_3 + H^+$. Is the reaction endothermic or exothermic if all concentrations are 0.01 M? Does the reaction proceed spontaneously as written if all concentrations are 1 M? For NH_4^+: $\overline{H}_f^o = -132.5$ kJ/mol, $\overline{S}_f^o = 113.4$ J/mol-°K, and $\overline{G}_f^o = -79.37$ kJ/mol. For NH_3: $\overline{H}_f^o = -80.3$ kJ/mol, $\overline{S}_f^o = 111$ J/mol-°K, and $\overline{G}_f^o = -26.57$ kJ/mol. For H^+: $\overline{H}_f^o = 0$ kJ/mol, $\overline{S}_f^o = 0$ J/mol-°K, and $\overline{G}_f^o = 0$ kJ/mol.

Purpose of problem

Use of thermodynamic equations

Relevant section(s) of text

Section 3.7

Solution

To determine if the reaction is endothermic or exothermic, calculate ΔH_{rxn} assuming all concentrations are 0.01 M:

$$
\begin{aligned}
\Delta H_{rxn} &= [NH_3]\,\overline{H}_{f,NH_3}^o - [H^+]\,\overline{H}_{f,H^+}^o - [NH_4^+]\,\overline{H}_{f,NH_4^+}^o \\
&= [-80.3 \text{ kJ/mol} + 0 \text{ kJ/mol} - (-132.5 \text{ kJ/mol})](0.01 \text{ M}) \\
&= +0.522 \text{ kJ/L}
\end{aligned}
$$

Heat is absorbed ($\Delta Q_P = \Delta H_{rxn} > 0$) and therefore the reaction is endothermic if all concentrations are 0.01 M.

To determine if the reaction proceeds spontaneously, calculate ΔG_{rxn} assuming all concentrations are 0.01M:

$$
\begin{aligned}
\Delta G_{rxn} &= [NH_3]\,\overline{G}_{f,NH_3}^o - [H^+]\,\overline{G}_{f,H^+}^o - [NH_4^+]\,\overline{G}_{f,NH_4^+}^o \\
&= [-26.57 \text{ kJ/mol} + 0 \text{ kJ/mol} - (-79.37 \text{ kJ/mol})](0.01 \text{ M}) \\
&= +0.528 \text{ kJ/L}
\end{aligned}
$$

$\Delta G_{rxn} > 0$ and therefore the reaction does *not* proceed spontaneously as written (assuming that all concentrations are 0.01 M).

Problem 3.6

Calculate K for the reaction in Problem 3.4 at equilibrium. (At equilibrium, you cannot assume all species concentrations are 1 M.) At what pH are the equilibrium activities of HSO_4^- and SO_4^{2-} equal?

Purpose of problem

Test understanding of equilibrium and use of thermodynamic equations

Relevant section(s) of text

Section 3.9

Solution

From eq. 3.18: $K = \exp(-\Delta G_{rxn}^o / RT)$
From Problem 3.4: $\Delta G_{rxn}^o = +11.4$ kJ/mol
Thus, at 25°C (= 298°K):

$K = \exp[-(11.4 \text{ kJ/mol})/(8.314 \times 10^{-3} \text{ kJ/mole-°K})(298°\text{K})] = \mathbf{1.0 \times 10^{-2}}$

Also: $K = \{SO_4^{2-}\}\{H^+\}/\{HSO_4^-\}$

Thus, $\{SO_4^{2-}\} = \{HSO_4^-\}$ when $\{H^+\} = K = 1.0 \times 10^{-2}$ or pH $= -\log\{H^+\} = -\log(1.0 \times 10^{-2}) = \mathbf{2.0}$

Problem 3.7
Calculate K for the reaction in Problem 3.5 at equilibrium. (At equilibrium, you cannot assume all species concentrations are 0.01 M.) At what range of pH is $\{NH_4^+\} > \{NH_3\}$ at equilibrium?

Purpose of problem
Test understanding of equilibrium and use of thermodynamic equations

Relevant section(s) of text
Section 3.9

Solution
From eq. 3.18: $K = \exp(-\Delta G_{rxn}^o/RT)$
From Problem 3.5: $\Delta G_{rxn}^o = +52.8$ kJ/mol
Thus, at 25°C (= 298°K):

$$K = \exp[-(52.8 \text{ kJ/mol})/(8.314 \times 10^{-3} \text{ kJ/mole-}^o\text{K})(298^o\text{K})] = \mathbf{5.6 \times 10^{-10}}$$

Also: $K = \{NH_3\}\{H^+\}/\{NH_4^+\}$

Thus, $\{NH_4^+\} > \{NH_3\}$ when $\{H^+\} > K = 5.6 \times 10^{-10}$

This occurs when or pH $= -\log\{H^+\} < -\log(5.6 \times 10^{-10})$ or $\mathbf{pH < 9.3}$

(Note: $\{H^+\} > K \Rightarrow \log\{H^+\} > -\log K \Rightarrow \log\{H^+\} < -\log K$, since the inequality sign is reversed when you multiply both sides of an inequality by a negative number)

Problem 3.8
What is the criterion for equilibrium in terms of G? ΔG_{rxn}? ΔG^o_{rxn}?

Purpose of problem
Test understanding of equilibrium

Relevant section(s) of text
Sections 3.8 and 3.9

Solution
From the text:

G is minimized at equilibrium
$\Delta G_{rxn} = 0$ at equilibrium (since G is minimized)
$\Delta G^o_{rxn} = -RT\ln K$ at equilibrium

Problem 3.9
From the example discussed in Section 3.8.4, calculate the equilibrium constant for the equilibrium $O_2(g) = O_2(aq)$ from the equilibrium concentrations of $O_2(g)$ and $O_2(aq)$. How does your value compare to the accepted value of 1.26×10^{-3} mol/L-atm? (Be careful about units.) How does your value compare to that calculated from ΔG_{rxn}^o? (See Section 3.8.4 for concentrations and thermodynamic data.)

Purpose of problem
Calculation of K from species concentrations and the relationship between ΔG_{rxn}^o and K

Relevant section(s) of text
Section 3.9

Solution
The equilibrium is $O_2(g) = O_2(aq)$, so, assuming concentrations and activities: $K = [O_2(aq)]/[O_2(g)] = [O_2(aq)]/P_{O2}$

From Section 3.8.4, 2.79×10^{-4} mol of O_2 dissolves in 1 L of water at equilibrium. The atmosphere has a very large amount of oxygen, so assume P_{O2} remains at 0.209 at equilibrium. Thus:

$$K = [O_2(aq)]/P_{O2} = (2.79 \times 10^{-4} \text{ mol/L})/(0.209 \text{ atm}) = \mathbf{1.33 \times 10^{-3} \text{ mol/L-atm}}$$

This is within 6% of the accepted value.

The equilibrium constant also can be calculated from ΔG_{rxn}^o:

From the text (Section 3.84), $\overline{G}_f^o$ for $O_2(aq) = +16.32$ kJ/mol. Also, $\overline{G}_f^o$ for $O_2(g) = 0$, since oxygen is present as $O_2(g)$ in its standard state. Thus $\Delta G_{rxn}^o = +16.32$ kJ/mol and therefore $K = \exp(-\Delta G_{rxn}^o/RT) = \exp[(-16.32 \text{ kJ/mol})/(8.314 \times 10^{-3} \text{ kJ/mol-}^oK)(298.16^oK)] = \mathbf{1.38 \times 10^{-3}}$.

Problem 3.10
From the example discussed in Section 3.7.3, calculate the equilibrium constant for AgCl(s) =
$Ag^+ + Cl^-$. How does your value compare to the accepted value of 2.8×10^{-10}?

Purpose of problem
Calculation of K from species concentrations and the relationship between ΔG_{rxn}^o and K

Relevant section(s) of text
Section 3.9

Solution
From Section 3.7.3:

$$\Delta G_{rxn}^o = \overline{G}_{f,Ag^+}^o + \overline{G}_{f,Cl^-}^o - \overline{G}_{f,AgCl(s)}^o = +77.12 - 131.3 - (-109.8) = +55.6 \text{ kJ/mol}$$

Thus: $K = \exp(-\Delta G_{rxn}^o/RT)$
$= \exp[(-55.6 \text{ kJ/mol})/(8.314 \times 10^{-3} \text{ kJ/mol-}^o\text{K})(298.16^o\text{K})]$
$= \mathbf{1.8 \times 10^{-10}}$

This is within 36% of the accepted value.