## 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:

$$
\begin{aligned}
& d E=d H-P d V(\text { at constant pressure }), \text { or: } \\
& \Delta E=\Delta H-P \Delta V
\end{aligned}
$$

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

## Problem 3.2

To illustrate the relationship in Problem 3.1, calculate $\Delta H$ and $\Delta E$ when 100 g of ice melts at $25^{\circ} \mathrm{C}$ and 1 atm . How much heat is absorbed by the system? For ice: $\bar{H}_{f}^{o}=-292.80 \mathrm{~kJ} / \mathrm{mol}$ and molar volume $=0.0196 \mathrm{~L} / \mathrm{mol}$; for water: $\bar{H}_{f}^{o}=-285.83 \mathrm{~kJ} / \mathrm{mol}$ 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: $\mathrm{H}_{2} \mathrm{O}(\mathrm{s}) \rightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{l})$
We are interested in 100 g of ice $=(100 \mathrm{~g}) /(18 \mathrm{~g} / \mathrm{mol})=5.56$ moles of ice
$\Delta H=\bar{H}_{f, \text { water }}^{o}-\bar{H}_{f, \text { ice }}^{o}=-285.83-(-292.80)=6.97 \mathrm{~kJ} / \mathrm{mol}$ or 38.75 kJ for 5.56 moles
$\Delta V=\Delta V_{\text {water }}-\Delta V_{\text {ice }}=0.0180-0.0196=-0.0016 \mathrm{~L} / \mathrm{mol}$ or -0.0089 L for 5.56 moles
From eq. 3.2:
$\Delta E=\Delta H-P \Delta V=38.75 \mathrm{~kJ}-(1 \mathrm{~atm})(-0.0089 \mathrm{~L})(X \mathrm{~kJ} / \mathrm{L}-\mathrm{atm})$
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, $R=8.314 \times 10^{-3} \mathrm{~kJ} / \mathrm{mol}^{\circ} \mathrm{K}$ and $R^{\prime}=0.082057 \mathrm{~L}$ $\mathrm{atm} / \mathrm{mol}-{ }^{\circ} \mathrm{K}, X=0.1013 \mathrm{~kJ} / \mathrm{L}-\mathrm{atm}$.

So: $\Delta E=\Delta H-P \Delta V=38.75 \mathrm{~kJ}-(1 \mathrm{~atm})(-0.0089 \mathrm{~L})(0.1013 \mathrm{~kJ} / \mathrm{L}-\mathrm{atm}) \approx \mathbf{3 8 . 7 5} \mathbf{~ k J}$
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: $\Delta Q_{P}=+38.75 \mathrm{~kJ}$ and $38.75 \mathbf{~ k J}$ 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 $25^{\circ} \mathrm{C}$ and 1 atm? Assume graphite and diamond are incompressible. The $\bar{G}_{f}^{o}$ values are 0 and $-2.59 \mathrm{~kJ} / \mathrm{mol}$ and densities are 2.25 and $3.51 \mathrm{~g} / \mathrm{cm}^{3}$ 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 ( $>100,000 \mathrm{~atm}$ ) 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: $d G=V d P-S_{s y s} d T$
At constant temperature: $d G / d P=V$
Integrating for a chemical reaction: $\Delta G_{r x n}=P \Delta V_{r x n}$
where: $\Delta V_{r x n}$ 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) $\rightarrow \mathrm{C}$ (diamond)
We are interested in 1 g of graphite $=(1 \mathrm{~g}) /(12 \mathrm{~g} / \mathrm{mol})=0.0833$ mole of graphite

$$
\text { At } 25^{\circ} \mathrm{C}: \Delta G_{r x n}=\bar{G}_{f, \text { graphite }}^{o}-\bar{G}_{f, \text { diamond }}^{o}=-2.59-0=-2.59 \mathrm{~kJ} / \mathrm{mol} \text { or }-0.22 \mathrm{~kJ} \text { for } 0.0833 \text { mole }
$$

Also:

$$
\begin{aligned}
\Delta V_{r x n} & =\text { molar volume of diamond }- \text { molar volume of graphite } \\
& =(12 \mathrm{~g} / \mathrm{mol}) /(3510 \mathrm{~g} / \mathrm{L})-(12 \mathrm{~g} / \mathrm{mol}) /(2250 \mathrm{~g} / \mathrm{L}) \\
& =-1.91 \mathrm{~L} / \mathrm{mol} \text { or }-1.59 \times 10^{-4} \mathrm{~L} \text { for } 0.0833 \mathrm{~mole}
\end{aligned}
$$

Thus:
$\Delta G_{r x n}=P \Delta V_{r x n}$ or:
$P=\Delta G_{r x n} / \Delta V_{r x n}$

$$
=(-0.22 \mathrm{~kJ}) /\left(-1.59 \times 10^{-4} \mathrm{~L}\right)=1384 \mathrm{~kJ} / \mathrm{L}
$$

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

So: $P($ in atm $)=(1384 \mathrm{~kJ} / \mathrm{L}) /(0.1013 \mathrm{~kJ} / \mathrm{L}-\mathrm{atm})=13,660 \mathrm{~atm}$

## So graphite will equilibrate with the diamond phase at about $14,000 \mathrm{~atm}$

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: $\mathrm{HSO}_{4}{ }^{-} \rightarrow \mathrm{SO}_{4}{ }^{2-}+\mathrm{H}^{+}$. 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 $\mathrm{HSO}_{4}{ }^{-}: \bar{H}_{f}^{o}=-887.3 \mathrm{~kJ} / \mathrm{mol}, \bar{S}_{f}^{o}=132 \mathrm{~J} / \mathrm{mol}^{-}{ }^{\circ} \mathrm{K}$, and $\bar{G}_{f}^{o}=-756.0 \mathrm{~kJ} / \mathrm{mol}$. For $\mathrm{SO}_{4}{ }^{2-}: \bar{H}_{f}^{o}=-909.2 \mathrm{~kJ} / \mathrm{mol}, \bar{S}_{f}^{o}=20.1 \mathrm{~J} / \mathrm{mol}^{\circ} \mathrm{K}$, and $\bar{G}_{f}^{o}=-744.6 \mathrm{~kJ} / \mathrm{mol}$. For $\mathrm{H}^{+}: \bar{H}_{f}^{o}=0$ $\mathrm{kJ} / \mathrm{mol}, \bar{S}_{f}^{o}=0 \mathrm{~J} / \mathrm{mol}-{ }^{\circ} \mathrm{K}$, and $\bar{G}_{f}^{o}=0 \mathrm{~kJ} / \mathrm{mol}$.

## 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 $\Delta H_{r x n}^{o}$ assuming all concentrations are 1 M :

$$
\Delta H_{r x n}^{o}=\bar{H}_{f, S O_{4}^{2-}}^{o}-\bar{H}_{f, H^{+}}^{o}-\bar{H}_{f, H S O_{4}^{-}}^{o}=-909.2+0-(-887.3)=-21.9 \mathrm{~kJ} / \mathrm{mol}
$$

Heat is released $\left(\Delta Q_{P}=\Delta H_{r x n}^{0}<0\right)$ and therefore the reaction is exothermic if all concentrations are 1 M .

To determine if the reaction proceeds spontaneously, calculate $\Delta G_{r x n}^{0}$ assuming all concentrations are 1 M :

$$
\Delta G_{r x n}^{o}=\bar{G}_{f, S O_{4}^{2_{-}^{2-}}}^{o}-\bar{G}_{f, H^{+}}^{o}-\bar{G}_{f, H S O_{4}^{-}}^{o}=-744.6+0-(-756.0)=+11.4 \mathrm{~kJ} / \mathrm{mol}
$$

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

## Problem 3.5

Consider the reaction: $\mathrm{NH}_{4}{ }^{+} \rightarrow \mathrm{NH}_{3}+\mathrm{H}^{+}$. 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 $\mathrm{NH}_{4}{ }^{+}: \bar{H}_{f}^{o}=-132.5 \mathrm{~kJ} / \mathrm{mol}, \bar{S}_{f}^{o}=113.4 \mathrm{~J} / \mathrm{mol}{ }^{\circ} \mathrm{K}$, and $\bar{G}_{f}^{o}=-79.37$ $\mathrm{kJ} / \mathrm{mol}$. For $\mathrm{NH}_{3}: \bar{H}_{f}^{o}=-80.3 \mathrm{~kJ} / \mathrm{mol}, \bar{S}_{f}^{o}=111 \mathrm{~J} / \mathrm{mol}-{ }^{\circ} \mathrm{K}$, and $\bar{G}_{f}^{o}=-26.57 \mathrm{~kJ} / \mathrm{mol}$. For $\mathrm{H}^{+}: \bar{H}_{f}^{o}=$ $0 \mathrm{~kJ} / \mathrm{mol}, \bar{S}_{f}^{o}=0 \mathrm{~J} / \mathrm{mol}^{\circ}{ }^{\circ} \mathrm{K}$, and $\bar{G}_{f}^{o}=0 \mathrm{~kJ} / \mathrm{mol}$.

## 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 $\Delta H_{r x n}$ assuming all concentrations are 0.01 M :

$$
\begin{aligned}
\Delta H_{r x n} & =\left[\mathrm{NH}_{3}\right] \bar{H}_{f, N H_{3}}^{o}-\left[\mathrm{H}^{+}\right] \bar{H}_{f, H^{+}}^{o}-\left[\mathrm{NH}_{4}^{+}\right] \bar{H}_{f, N H_{4}^{+}}^{o} \\
& =[-80.3 \mathrm{~kJ} / \mathrm{mol}+0 \mathrm{~kJ} / \mathrm{mol}-(-132.5 \mathrm{~kJ} / \mathrm{mol})](0.01 \mathrm{M}) \\
& =+0.522 \mathrm{~kJ} / \mathrm{L}
\end{aligned}
$$

Heat is absorbed $\left(\Delta Q_{P}=\Delta H_{r x n}>0\right)$ and therefore the reaction is endothermic if all concentrations are 0.01 M .

To determine if the reaction proceeds spontaneously, calculate $\Delta G_{r x n}$ assuming all concentrations are 0.01 M :

$$
\begin{aligned}
\Delta G_{r x n} & =\left[\mathrm{NH}_{3}\right] \bar{G}_{f, N H_{3}}^{o}-\left[\mathrm{H}^{+}\right] \bar{G}_{f, H^{+}}^{o}-\left[\mathrm{NH}_{4}{ }^{+}\right] \bar{G}_{f, N H_{4}^{+}}^{o} \\
& =[-26.57 \mathrm{~kJ} / \mathrm{mol}+0 \mathrm{~kJ} / \mathrm{mol}-(-79.37 \mathrm{~kJ} / \mathrm{mol})](0.01 \mathrm{M}) \\
& =+0.528 \mathrm{~kJ} / \mathrm{L}
\end{aligned}
$$

$\Delta G_{r x n}>0$ 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 $\mathrm{HSO}_{4}^{-}$and $\mathrm{SO}_{4}{ }^{2-}$ 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: $K=\exp \left(-\Delta G_{r x n}^{0} / R T\right)$
From Problem 3.4: $\Delta G_{r x n}^{\mathrm{o}}=+11.4 \mathrm{~kJ} / \mathrm{mol}$
Thus, at $25^{\circ} \mathrm{C}\left(=298^{\circ} \mathrm{K}\right)$ :

$$
K=\exp \left[-(11.4 \mathrm{~kJ} / \mathrm{mol}) /\left(8.314 \times 10^{-3} \mathrm{~kJ} / \mathrm{mole}^{-}{ }^{\mathrm{O}} \mathrm{~K}\right)\left(298^{\circ} \mathrm{K}\right)\right]=\mathbf{1 . 0} \times \mathbf{1 0}^{-\mathbf{2}}
$$

Also: $K=\left\{\mathrm{SO}_{4}{ }^{2-}\right\}\left\{\mathrm{H}^{+}\right\} /\left\{\mathrm{HSO}_{4}{ }^{-}\right\}$
Thus, $\left\{\mathrm{SO}_{4}{ }^{2-}\right\}=\left\{\mathrm{HSO}_{4}^{-}\right\}$when $\left\{\mathrm{H}^{+}\right\}=K=1.0 \times 10^{-2}$ or $\mathrm{pH}=-\log \left\{\mathrm{H}^{+}\right\}=-\log \left(1.0 \times 10^{-2}\right)=\mathbf{2 . 0}$

## 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 $\left\{\mathrm{NH}_{4}{ }^{+}\right\}>\left\{\mathrm{NH}_{3}\right\}$ 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: $K=\exp \left(-\Delta G_{r x n}^{\mathrm{o}} / R T\right)$
From Problem 3.5: $\Delta G_{r x n}^{\mathrm{o}}=+52.8 \mathrm{~kJ} / \mathrm{mol}$
Thus, at $25^{\circ} \mathrm{C}\left(=298^{\circ} \mathrm{K}\right)$ :

$$
K=\exp \left[-(52.8 \mathrm{~kJ} / \mathrm{mol}) /\left(8.314 \times 10^{-3} \mathrm{~kJ} / \mathrm{mole}^{-}{ }^{\circ} \mathrm{K}\right)\left(298^{\circ} \mathrm{K}\right)\right]=\mathbf{5 . 6}^{\times 10^{-10}}
$$

Also: $K=\left\{\mathrm{NH}_{3}\right\}\left\{\mathrm{H}^{+}\right\} /\left\{\mathrm{NH}_{4}{ }^{+}\right\}$
Thus, $\left\{\mathrm{NH}_{4}{ }^{+}\right\}>\left\{\mathrm{NH}_{3}\right\}$ when $\left\{\mathrm{H}^{+}\right\}>K=5.6 \times 10^{-10}$
This occurs when or $\mathrm{pH}=-\log \left\{\mathrm{H}^{+}\right\}<-\log \left(5.6 \times 10^{-10}\right)$ or $\mathbf{p H}<\mathbf{9 . 3}$
(Note: $\left\{\mathrm{H}^{+}\right\}>K=>\log \left\{\mathrm{H}^{+}\right\}>-\log K=>\log \left\{\mathrm{H}^{+}\right\}<-\log K$, 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 $G ? \Delta G_{r x n}$ ? $\Delta G_{r x n}^{\mathrm{o}}$ ?

## 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
$\Delta G_{r \times n}=0$ at equilibrium (since $G$ is minimized)
$\Delta G_{r x n}^{0}=-R T \ln K$ at equilibrium

## Problem 3.9

From the example discussed in Section 3.8.4, calculate the equilibrium constant for the equilibrium $\mathrm{O}_{2}(\mathrm{~g})=\mathrm{O}_{2}(\mathrm{aq})$ from the equilibrium concentrations of $\mathrm{O}_{2}(\mathrm{~g})$ and $\mathrm{O}_{2}(\mathrm{aq})$. How does your value compare to the accepted value of $1.26 \times 10^{-3} \mathrm{~mol} / \mathrm{L}-\mathrm{atm}$ ? (Be careful about units.) How does your value compare to that calculated from $\Delta G_{r x n}^{\mathrm{o}}$ ? (See Section 3.8.4 for concentrations and thermodynamic data.)

## Purpose of problem

Calculation of $K$ from species concentrations and the relationship between $\Delta G_{r x n}^{\mathrm{o}}$ and $K$

## Relevant section(s) of text

Section 3.9

## Solution

The equilibrium is $\mathrm{O}_{2}(\mathrm{~g})=\mathrm{O}_{2}(\mathrm{aq})$, so, assuming concentrations and activities: $K=$ $\left[\mathrm{O}_{2}(\mathrm{aq})\right] /\left[\mathrm{O}_{2}(\mathrm{~g})\right]=\left[\mathrm{O}_{2}(\mathrm{aq})\right] / \mathrm{P}_{\mathrm{O} 2}$

From Section 3.8.4, $2.79 \times 10^{-4} \mathrm{~mol}$ of $\mathrm{O}_{2}$ dissolves in 1 L of water at equilibrium. The atmosphere has a very large amount of oxygen, so assume $P_{\mathrm{O} 2}$ remains at 0.209 at equilibrium. Thus:

$$
K=\left[\mathrm{O}_{2}(\mathrm{aq})\right] / P_{O 2}=\left(2.79 \times 10^{-4} \mathrm{~mol} / \mathrm{L}\right) /(0.209 \mathrm{~atm})=\mathbf{1 . 3 3} \times \mathbf{1 0}^{-\mathbf{3}} \mathbf{~ m o l} / \mathbf{L}-\mathbf{a t m}
$$

This is within $6 \%$ of the accepted value.
The equilibrium constant also can be calculated from $\Delta G_{r x n}^{\mathrm{o}}$ :
From the text (Section 3.84), $\bar{G}_{f}^{o}$ for $\mathrm{O}_{2}(\mathrm{aq})=+16.32 \mathrm{~kJ} / \mathrm{mol}$. Also, $\bar{G}_{f}^{o}$ for $\mathrm{O}_{2}(\mathrm{~g})=0$, since oxygen is present as $\mathrm{O}_{2}(\mathrm{~g})$ in its standard state. Thus $\Delta G_{r x n}^{\mathrm{o}}=+16.32 \mathrm{~kJ} / \mathrm{mol}$ and therefore $K$ $=\exp \left(-\Delta G_{r x n}^{\mathrm{o}} / R T\right)=\exp \left[(-16.32 \mathrm{~kJ} / \mathrm{mol}) /\left(8.314 \times 10^{-3} \mathrm{~kJ} / \mathrm{mol}^{\circ}{ }^{\circ} \mathrm{K}\right)\left(298.16^{\circ} \mathrm{K}\right)\right]=\mathbf{1 . 3 8}^{\mathbf{o}} \mathbf{1 0}^{-3}$.

## Problem 3.10

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

## Purpose of problem

Calculation of $K$ from species concentrations and the relationship between $\Delta G_{r x n}^{0}$ and $K$

## Relevant section(s) of text

Section 3.9

## Solution

From Section 3.7.3:

$$
\Delta G_{r x n}^{o}=\bar{G}_{f, A g^{+}}^{o}+\bar{G}_{f, C l^{-}}^{o}-\bar{G}_{f, A g C l(s)}^{o}=+77.12-131.3-(-109.8)=+55.6 \mathrm{~kJ} / \mathrm{mol}
$$

Thus: $K=\exp \left(-\Delta G_{r x n}^{\mathrm{o}} / R T\right)$

$$
\begin{aligned}
& =\exp \left[(-55.6 \mathrm{~kJ} / \mathrm{mol}) /\left(8.314 \times 10^{-3} \mathrm{~kJ} / \mathrm{mol}^{\circ} \mathrm{K}\right)\left(298.16^{\circ} \mathrm{K}\right)\right] \\
& =\mathbf{1 . 8} \times \mathbf{1 0}^{-\mathbf{1 0}}
\end{aligned}
$$

This is within $36 \%$ of the accepted value.

