Solutions to CHM 4411 Homework 10

Give reference to tabular data used

1. A general condition for equilibrium in an isolated system is \( dS = 0 \).

So, let \( a \) and \( b \) be two phases of an isolated system in thermal contact with each other. Then,

\[
dS = dS_a + dS_b = 0.
\]

Entropy is an additive property and may be expressed in terms of internal energy \( U \) and volume \( V \):

\[
S = S(U,V).
\]

Assuming \( dV_a = 0 \) and \( dV_b = 0 \), we write

\[
dS = \left( \frac{\partial S_a}{\partial U_a} \right)_V dU_a + \left( \frac{\partial S_b}{\partial U_b} \right)_V dU_b = \frac{1}{T_a} dU_a + \frac{1}{T_b} dU_b.
\]

and since \( dU_a = -dU_b \) it follows that \( T_a = T_b \).

Allowing the volume of the phases to change, but system still in equilibrium, means that \( dU_a = -dU_b \) and \( dV_a = -dV_b \). We write

\[
dS = \left( \frac{\partial S_a}{\partial U_a} \right)_{V_a} dU_a + \left( \frac{\partial S_b}{\partial U_b} \right)_{V_b} dU_b + \left( \frac{\partial S_a}{\partial V_a} \right)_{U_a} dV_a + \left( \frac{\partial S_b}{\partial V_b} \right)_{U_b} dV_b
\]

and, thus

\[
dS = \left( \frac{1}{T_a} - \frac{1}{T_b} \right) dU_a + \left( \frac{p_a}{T_a} - \frac{p_b}{T_b} \right) dV_a = 0.
\]

This can be satisfied in general only if \( T_a = T_b \), and \( p_a/T_a = p_b/T_b \), which leads to \( T_a = T_b \) and \( p_a = p_b \).

2. The equilibrium constant for

\[
A \rightleftharpoons B
\]
is

\[ K = \frac{a_B}{a_A} \approx \frac{\gamma_B x_B}{\gamma_A x_A} \]

in terms of mole fractions. A reasonable assumption for isomers is that \( \gamma_A \approx \gamma_B \), which leads to the two equations \( x_B = x_A \times K \) and \( x_A + x_B = 1 \).

\[ K = \exp -\Delta_r G^\circ / RT = \exp 2.2 \times 10^3/(8.314 \times 310) = 2.35, \]

so \( x_A = 1/3.34 = 0.30 \) and \( x_B = 0.70 \).

3. Given the rate law

\[ \frac{d[A]}{dt} = -k[A]^n \]

we get

\[ -\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^n} = k \int_0^t dt \]

or

\[ k t = \left[ \frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}} \right] \times \frac{1}{(n-1)} \]

Then \([A]_0 \) goes to \([A]_0/3 \) in

\[ t_{1/3} = \left[ \frac{3^{n-1}}{[A]_0^{n-1}} - \frac{1}{[A]_0^{n-1}} \right] \times \frac{1}{k(n-1)} \]

seconds.

4. The give equilibrium \( A \rightleftharpoons B + C \) has the rate equation

\[ \frac{dx}{dt} = \frac{d[A]}{dt} = -k_f(x + [A]_{eq}) + k_r(-x + [B]_{eq})(-x + [C]_{eq}). \]

With the equilibrium condition \( k_f[A]_{eq} = k_r[B]_{eq}[C]_{eq} \), and neglecting \( x^2 \) terms, we get
\[
\frac{dx}{dt} = -(k_f + k_r[B]_{eq} + k_r[C]_{eq})x,
\]
which has the solution \( x = x_0 e^{-t/\tau} \), with

\[
\frac{1}{\tau} = [k_f + k_r[B]_{eq} + k_r[C]_{eq}].
\]

We can also involve the equilibrium constant \( K \) to write

\[
k_f = k_r \times K = \frac{1}{\tau} - k_r([B]_{eq} + [C]_{eq}),
\]
or

\[
k_r = \frac{1}{\tau(K + [B]_{eq} + [C]_{eq})}
\]

\[
= \frac{1}{(3.0 \times 10^{-6}s) \times (2.0 \times 10^{-4} + 2 \times 5.0 \times 10^{-4})\text{molL}^{-1}]}^{-1} \tag{1}
\]

\[
= 2.78 \times 10^8\text{Lmol}^{-1}\text{s}^{-1},
\]

and

\[
k_f = K \times k_r = 2.0 \times 10^{-4}\text{molL}^{-1} \times 2.78 \times 10^8\text{Lmol}^{-1}\text{s}^{-1} \tag{2}
\]

\[
= 5.56 \times 10^4 = \text{s}^{-1}.
\]