

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

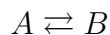
$$dS = \left(\frac{\partial S_a}{\partial U_a} \right)_{V_a} dU_a + \left(\frac{\partial S_b}{\partial U_b} \right)_{V_b} dU_b + \left(\frac{\partial S_a}{\partial V_a} \right)_{U_a} dV_a + \left(\frac{\partial S_b}{\partial V_b} \right)_{U_b} dV_b$$

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



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 $x_A + x_B = 1$.

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

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

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

or

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

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

$$\begin{aligned} k_r &= \frac{1}{\tau(K + [B]_{eq} + [C]_{eq})} \\ &= [(3.0 \times 10^{-6}\text{s}) \times (2.0 \times 10^{-4} + 2 \times 5.0 \times 10^{-4})\text{molL}^{-1}]^{-1} \quad (1) \\ &= 2.78 \times 10^8 \text{Lmol}^{-1}\text{s}^{-1}, \end{aligned}$$

and

$$\begin{aligned} k_f &= K \times k_r = 2.0 \times 10^{-4}\text{molL}^{-1} \times 2.78 \times 10^8 \text{Lmol}^{-1}\text{s}^{-1} \quad (2) \\ &= 5.56 \times 10^4 = \text{s}^{-1}. \end{aligned}$$