Chemistry 2740 Spring 2008 Test 3 Solutions

1. The law of microscopic reversibility says that every elementary reaction is reversible. This implies that both the forward and reverse of an elementary reaction occur at the same time. In particular, in equilibrium the forward and reverse of a reaction are occurring at the same rate. This is what we mean by dynamic equilibrium: Reactions are still going on, but the net rate of reaction is zero.

2. Figure 1 shows diagrams and provides brief descriptions of all three methods discussed in the textbook. Comparing these methods may involve any of the following points:

   - Method (c) is the fastest of the 3, followed by (b), with (a) being the slowest.
   - Method (b) provides the largest pressure jumps, followed by (a), with (c) allowing the smallest pressure jumps. Since the change in the equilibrium constant depends on the change in pressure, (b) will provide the largest changes, which gives us a bit more recording time before the reaction returns to equilibrium, and (c) the least, with (a) being intermediate.
   - Method (c) creates a downward pressure jump to ambient pressure. Method (a) creates upward pressure jumps, typically to very large pressures. Method (b) can be used to vary the pressure up or down. Methods (b) and (c) are thus most appropriate if we want to relate the kinetic data obtained to (e.g.) thermodynamic data tabulated at 1 bar. Method (b) allows us to measure rate constants at a variety of pressures, from ambient up to a few hundred atmospheres.

3. (a)

$$
\begin{aligned}
K &= \frac{k_a}{k_d} \\
\therefore k_d &= \frac{k_a}{K} = \frac{2.4 \times 10^{11}\,\mathrm{L\,mol^{-1}s^{-1}}}{8.1 \times 10^{12}\,\mathrm{L/mol}} = 0.030\,\mathrm{s^{-1}}
\end{aligned}
$$

(b)

$$
\begin{aligned}
v &= k_a[\mathrm{NiL}^{2+}][\mathrm{CH_3CN}] \\
&= (2.4 \times 10^{11}\,\mathrm{L\,mol^{-1}s^{-1}})(1.0 \times 10^{-11}\,\mathrm{mol/L})(1.7 \times 10^{-11}\,\mathrm{mol/L}) \\
&= 4.1 \times 10^{-11}\,\mathrm{mol\,L^{-1}s^{-1}}
\end{aligned}
$$

(c)

$$
\begin{aligned}
v &\approx \frac{\Delta[\mathrm{NiL}^{2+} \cdot \mathrm{CH_3CN}]}{\Delta t} \\
\therefore \Delta t &\approx \frac{\Delta[\mathrm{NiL}^{2+} \cdot \mathrm{CH_3CN}]}{v} \\
&= \frac{1 \times 10^{-14}\,\mathrm{mol/L}}{4.1 \times 10^{-11}\,\mathrm{mol\,L^{-1}s^{-1}}} = 0.0002\,\mathrm{s}
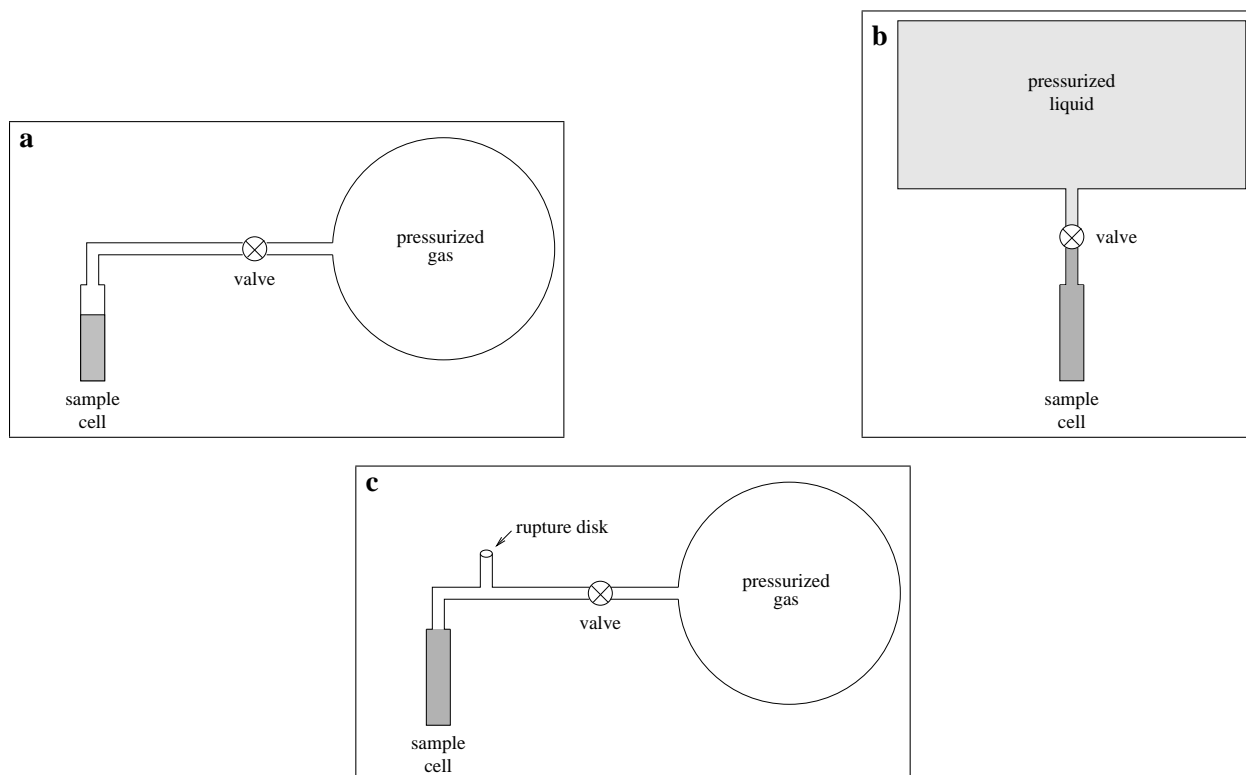\end{aligned}
$$

Figure 1: Methods for creating a pressure jump. (a) A valve is opened to a pressurized gas cylinder. (b) A valve is opened to a pressurized liquid ballast. Note that the sample cell in this case is filled right up to the valve such that the pressure is transmitted through the liquid. (c) The sample cell is pressurized slowly using a compressed gas. A rapid downward pressure jump is obtained by breaking a rupture disk.
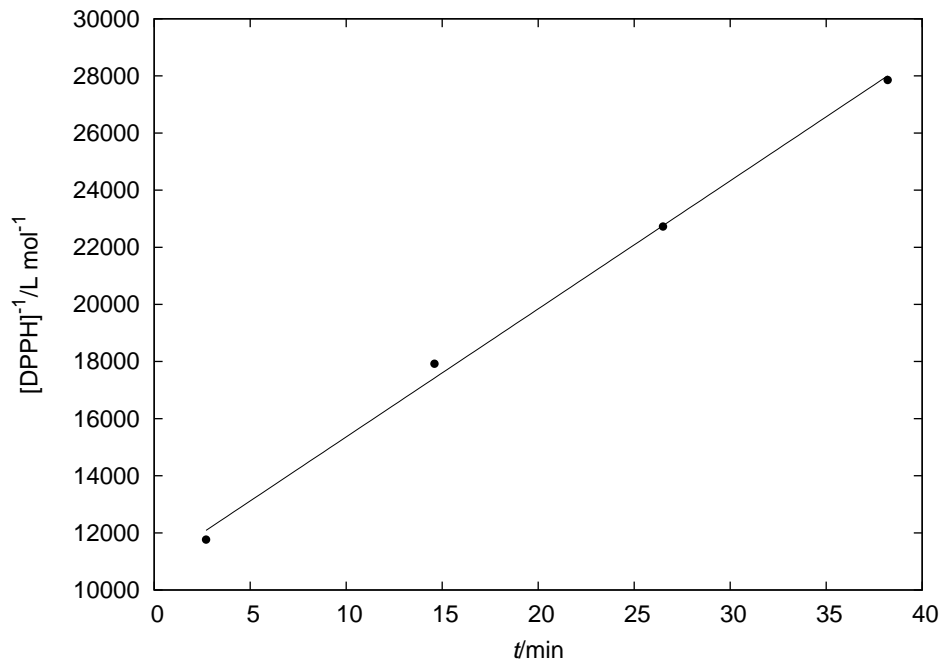
Figure 2: Second-order plot for the reaction of DPPH with polyphenylene.

4. (a) We will apply the steady-state approximation to the intermediate $\{PP \cdot DPPH\}$:

$$\frac{d[\{PP \cdot DPPH\}]}{dt} = k_1[PP][DPPH] - k_{-1}[\{PP \cdot DPPH\}] - k_2[\{PP \cdot DPPH\}][DPPH] \approx 0.$$

$$\therefore [\{PP \cdot DPPH\}] \approx \frac{k_1[PP][DPPH]}{k_{-1} + k_2[DPPH]}.$$

The rate of reaction is
$$v = k_2[\{PP \cdot DPPH\}][DPPH].$$

Using our expression for the intermediate concentration, we get

$$v \approx \frac{k_1 k_2 [PP][DPPH]^2}{k_{-1} + k_2[DPPH]}.$$

If $k_2[DPPH] \ll k_{-1}$, then this rate law reduces to

$$v \approx \frac{k_1 k_2}{k_{-1}}[PP][DPPH]^2.$$

(b) If it's a second-order reaction, a plot of $1/[DPPH]$ vs t should be linear. My graph is shown in figure 2. The graph is linear, so the reaction does obey second-order kinetics. The slope of the graph (obtained by linear regression) is

$$k = 448 \, \text{L} \, \text{mol}^{-1} \text{min}^{-1}.$$

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