Chemistry 230 — Fall 2001
Exam 3B Solutions

NAME: KEY
(please print)

CHEMISTRY 230 — Tellinghuisen
Third Exam – Part B — 12/6/01

Honor Code Pledge and Signature:

Fundamental Constants: $R = 8.31451$ J mol^{-1} K^{-1} = 0.0820578 L atm mol^{-1} K^{-1} = 1.9872 cal mol^{-1} K^{-1}
$N_A = 6.02214 \times 10^{23}$ mol^{-1}

I. (20) Reaction Kinetics. The reaction, $2\,A + B \rightarrow C + 3\,D$, is second order in A, first order in B.

A. Write the rate law for the forward reaction, using k for the rate constant.

$$r = k[A]^2[B]$$

B. Give expressions for the rates of change of concentration with time, $d[A]/dt$, $d[B]/dt$, and $d[D]/dt$ in terms of the rate constant k and the appropriate concentrations. (Consider just the forward reaction.)

$$r = \frac{1}{\nu_i}\frac{d[A_i]}{dt} \Rightarrow \frac{d[A]}{dt} = -2k[A]^2[B]\ ; \quad \frac{d[B]}{dt} = -k[A]^2[B]$$

$$\frac{d[D]}{dt} = 3k[A]^2[B]$$

C. If concentrations are in units mol/L, what are the units of k ?

$$L^2\ mol^{-2}\ s^{-1}$$

D. If this reaction were an elementary reaction, what would the rate law be for the reverse reaction? Why is it virtually certain that this is not an elementary reaction?

$r_b = k_b[C][D]^3$. This is 4th order and would imply 4-way collisions — virtually impossible

E. Suppose that $k = 1.3 \times 10^{-2}$ in units appropriate for concentrations in mol/L and time in s. If the initial concentrations are $[A]_0 = 2.00$ mol/L and $[B]_0 = 0.040$ mol/L, calculate the half-life of the reaction. (**Hint:** Use the concept of pseudo order.)

$[A]_0 \gg [B]_0$, so $[A] \approx$ const $= [A]_0 \rightarrow k_{eff} = k[A]_0^2$

R_x is now pseudo-first order: $[B] = [B]_0 e^{-k_{eff}t}$

$$t_{1/2} = \frac{\ln 2}{k_{eff}} = 13._3\ s$$

F. Repeat the half-life calculation for the initial concentrations, $[A]_0 = 0.040$ mol/L and $[B]_0 = 2.00$ mol/L.

Now $[B]_0 \gg [A]_0$, so $[B] \approx [B]_0 \Rightarrow k'_{eff} = k[B]_0$

R_x is now pseudo-2nd order: $\frac{1}{[A]} - \frac{1}{[A]_0} = 2k'_{eff}t$

$$t_{1/2} = \frac{1}{[A]_0 \times (2k'_{eff})} = 4.8_1 \times 10^2\ s$$

II. (10) Mathematical Kinetics. Consider the elementary reaction $A \rightleftarrows 2\,C$.

A. Considering both forward (k_f) and reverse (k_b) reactions, obtain an expression for $d[A]/dt$ in terms of [A] and [C]. Then take the initial concentrations $[A]_0 = a$ and $[C]_0 = 0$, and express [A] as $[A] = a - x$. Obtain an equation for dx/dt.

$$\frac{d[A]}{dt} = -k_f[A] + k_b[C]^2 = -k_f(a-x) + k_b(2x)^2$$

$$\frac{d[A]}{dt} = \frac{d(a-x)}{dt} = -\frac{dx}{dt} \Rightarrow \boxed{\frac{dx}{dt} = k_f(a-x) - 4k_b x^2}$$

B. Now consider the reaction at equilibrium. Express $[C]_{eq}$ in terms of $[A]_{eq}$, k_f, and k_b.

$$r_f = r_b \Rightarrow k_f[A]_{eq} = k_b[C]_{eq}^2$$

$$\hookrightarrow [C]_{eq} = \left[\frac{k_f[A]_{eq}}{k_b}\right]^{1/2} = \{K_c[A]_{eq}\}^{1/2}$$

III. (10) Unimolecular Decomposition. To account for the unimolecular kinetics of decay, $A \rightarrow B$ (+ C), observed for many molecules in the gas phase, Lindemann proposed a two-step mechanism,

1. $A + M \rightleftarrows A^* + M$, followed by 2. $A^* \rightarrow B$ (+ C) .

In this scheme, A^* is an A molecule that has been energized physically by collision with M. Letting k_1 and k_{-1} represent the forward and reverse rates in the first step, and k_2 the second step, apply the steady-state approximation to A^* to obtain an expression for $r = d[B]/dt$. Use your results to discuss the behavior observed in the limits of high and low [M]. In particular, define k_{uni}, tell what conditions yield the observed unimolecular kinetics, and explain the "falloff" region.

A^* = "physical" intermediate. Set $\frac{d[A^*]}{dt} = 0 \Rightarrow$ solve for $[A^*]_{SS}$

$$\frac{d[A^*]}{dt} = k_1[A][M] - k_{-1}[A^*][M] - k_2[A^*]$$

$$\hookrightarrow [A^*]_{SS} = \frac{k_1[A][M]}{k_2 + k_{-1}[M]}$$

$$\hookrightarrow \frac{d[B]}{dt} = k_2[A^*] \approx k_2[A^*]_{SS} = \frac{k_2 k_1[A][M]}{k_2 + k_{-1}[M]}$$

$$\equiv k_{uni}[A]\ ; \quad k_{uni} \equiv \frac{k_1 k_2[M]}{k_2 + k_{-1}[M]}$$

High [M]: $k_{uni} \rightarrow \frac{k_1 k_2}{k_{-1}}$ — unimolecular kinetics

Low [M]: $\rightarrow k_1[M]$ — falloff (falls off with ↓[M])

IV. **(15) Solution Theory.** A *regular* binary solution is characterized by the following expressions for the chemical potentials:

$$\mu_A = \mu_A^* + RT\ln x_A + w\,x_B^2; \qquad \mu_B = \mu_B^* + RT\ln x_B + w\,x_A^2 .$$

A. Obtain expressions for the activity coefficients $\gamma_{I,A}$ and $\gamma_{I,B}$ for such a solution.

B. Assuming that w is independent of P and T, obtain expressions for ΔG_{mix} , G^E, and ΔV_{mix}.

C. Taking A to be solvent, what is $\gamma_{II,B}$?

A. $\mu_i = \mu_i^\circ + RT\ln a_i = \mu_i^* + RT\ln(\gamma_{I,i}\, x_i)$

[Conv. I]

$\hookrightarrow RT\ln(\gamma_{I,i}\, x_i) = RT(\ln\gamma_{I,i} + \ln x_i)$

$\hookrightarrow RT\ln\gamma_{I,A} = w x_B^2 \rightarrow \gamma_{I,A} = \exp\left[\frac{w x_B^2}{RT}\right]$

$\gamma_{I,B} = \exp\left[\frac{w x_A^2}{RT}\right]$

B. $\Delta G_{mix} = n_A(\mu_A - \mu_A^*) + n_B(\mu_B - \mu_B^*)$

$= nRT(x_A\ln x_A + x_B\ln x_B) + n w\, x_A x_B$

$G^E = G - G^{id} = \Delta G_{mix} - \Delta G_{mix}^{id} = n w x_A x_B$

$\Delta V_{mix} = \left(\frac{\partial\Delta G_{mix}}{\partial P}\right)_T = 0$ since w independent of T & P

C. $\gamma_{II,B} = \text{const} \times \gamma_{I,B}$, such that $\gamma_{II,B} \rightarrow 1$ as $x_B \rightarrow 0$.

$\ln\gamma_{II,B} = \ln(\text{const}) + \frac{w x_A^2}{RT}$

$\hookrightarrow \ln(\text{const}) = -\frac{w}{RT}$

$\hookrightarrow \gamma_{II,B} = \exp\left[\frac{w}{RT}(x_A^2 - 1)\right]$

Prob I ________

II ________

III ________