

NAME: _____
(please print)

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

Honor Code Pledge and Signature:

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

- I. (20) Reaction Kinetics.** The reaction, $2 \text{ A} + \text{ B} \rightarrow \text{ C} + 3 \text{ D}$, is second order in A, first order in B.
- A. Write the rate law for the forward reaction, using k for the rate constant.
- B. Give expressions for the rates of change of concentration with time, $d[\text{A}]/dt$, $d[\text{B}]/dt$, and $d[\text{D}]/dt$ in terms of the rate constant k and the appropriate concentrations. (Consider just the forward reaction.)
- C. If concentrations are in units mol/L, what are the units of k ?
- 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?
- 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 $[\text{A}]_0 = 2.00 \text{ mol/L}$ and $[\text{B}]_0 = 0.040 \text{ mol/L}$, calculate the half-life of the reaction. (**Hint:** Use the concept of pseudo order.)
- F. Repeat the half-life calculation for the initial concentrations, $[\text{A}]_0 = 0.040 \text{ mol/L}$ and $[\text{B}]_0 = 2.00 \text{ mol/L}$.

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

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 .

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

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,

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.

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

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

- A. Obtain expressions for the activity coefficients γ_{A} and γ_{B} for such a solution.
- B. Assuming that w is independent of P and T , obtain expressions for G_{mix} , G^E , and V_{mix} .
- C. Taking A to be solvent, what is γ_{B} ?

Prob I _____

II _____

III _____

IV _____

