I. (20) Reaction Kinetics. The reaction, $2A + B \rightarrow C + 3D$, 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, $\frac{d[A]}{dt}$, $\frac{d[B]}{dt}$, and $\frac{d[D]}{dt}$ 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 $[A]_0 = 2.00$ mol/L and $[B]_0 = 0.040$ mol/L, calculate the half-life of the reaction. (Hint: Use the concept of pseudo order.)

F. Repeat the half-life calculation for the initial concentrations, $[A]_0 = 0.040$ mol/L and $[B]_0 = 2.00$ mol/L.
II. (10) **Mathematical Kinetics.** Consider the elementary reaction \( A \rightleftharpoons 2 \text{C} \).

A. Considering both forward \((k_f)\) and reverse \((k_b)\) reactions, obtain an expression for \( \frac{d[A]}{dt} \) 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 \( \frac{dx}{dt} \).

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, \( A \rightarrow \text{B} (+ \text{C}) \), observed for many molecules in the gas phase, Lindemann proposed a two-step mechanism,

1. \( A + M \rightleftharpoons A^* + M \), followed by
2. \( A^* \rightarrow \text{B} (+ \text{C}) \).

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 \( r = \frac{d[B]}{dt} \). 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 \( \gamma_{IA} \) and \( \gamma_{IB} \) for such a solution.

B. Assuming that \( w \) is independent of \( P \) and \( T \), obtain expressions for \( \Delta G_{\text{mix}} \), \( G^E \), and \( \Delta V_{\text{mix}} \).

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