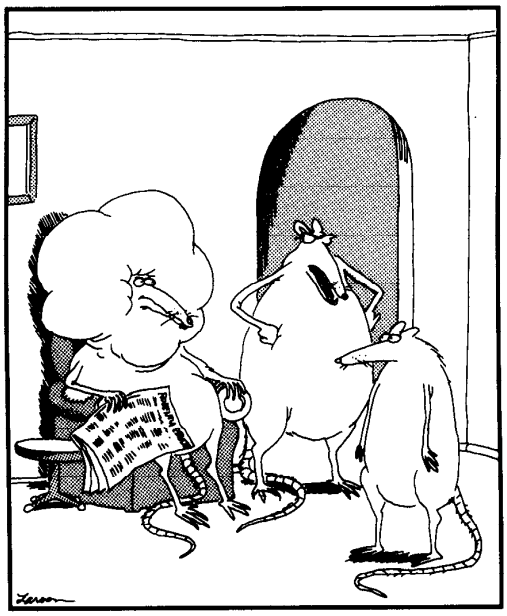
5.60

EXAM III

December 2, 2005



"Quit school? *Quit school?* You wanna end up like your father? A career lab rat?"

NAME: _____

This exam will be **closed book** and **closed notes**, but you will be permitted to use three 8.5" × 11" double-sided sheets of equations.

Material covered

- Lectures 22-30
- Problem Sets 7-9

GRADING:

I.	_____ / 20
II.	_____ / 20
III.	_____ / 30
IV.	_____ / 30 + 3
TOTAL:	_____ /100 + 3

I. Kinetics: Initial Rates (20 points)

Consider the recombination reaction

$$3A(g) + M(g) \rightarrow A_3(g) + M(g)$$

The empirical rate law is believed to have the form

$$\frac{dp_{A_3}}{dt} = k p_M^{\alpha} p_{A_2}^{\beta} p_A^{\gamma}$$

where p is pressure (in bar) and α, β, γ are the orders with respect to M, A_2, and A, which are to be determined by initial rate data. [NOTE that A_2 is not a typo! The species A_2 is found empirically to be involved in the reaction mechanism.]

A. (5 points) The rate of the reaction can be monitored by observing either $\frac{dp_A}{dt}$ or $\frac{dp_{A_3}}{dt}$. What is the relationship between $\frac{dp_A}{dt}$ and $\frac{dp_{A_3}}{dt}$ imposed by the reaction stoichiometry?

B. (5 points) What are the units of k for the empirical rate law as written?

C. (10 points) The observed initial rates obtained from measurements of p_{A_3} at $t = \tau$ and at $t = 0$ initial pressures (designated by p°) are:

p_A°/bar	$p_{A_2}^\circ$/bar	p_M°/bar	$\left.\frac{p_{A_3}(\tau) - p_{A_3}^\circ}{\tau}\right/ \text{bar}\cdot\text{s}^{-1}$
0.01	0.01	1.00	1.0
0.02	0.01	1.00	4.0
0.02	0.02	1.00	8.0
0.02	0.01	0.50	2.0

What are the values of α, β, γ, and k?

II. Colligative Properties (20 points)

The following numerical data may be useful:

molecular weight of water: 18g/mol

at p = 1 bar:

$T_b(H_2O) = 100°C$ $\Delta H_{vap}(H_2O) = 40kJ/mol$

$T_f(H_2O) = 0°C$ $\Delta H_{fusion}(H_2O) = 6.0kJ/mol$

A. (9 points) 1g of a pure crystalline substance A (ammonium acetate) known to have a molecular weight of 7.7×10^{-2} kg is dissolved in 1.0 kg of pure H_2O. What is the expected freezing point depression, in °C?

B. (5 points) Your answer to part **A** is based on several assumptions. What are those assumptions?

C. (3 points) If the observed freezing point depression is larger than your prediction in part **A**, what is the most likely reason for this departure from the standard model for colligative properties?

D. (3 points) If the first ice crystals formed at the depressed freezing point are found to have a concentration of A comparable to that in the initially made up solution, would this lead you to expect a freezing point depression larger or smaller than the standard colligative model? Why?

III. Kinetics: Steady State (30 points)

Consider the reaction

$$2A + B \rightarrow D.$$

Suppose that the mechanism of this reaction is found to consist of the elementary reactions

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C$$
$$A + C \xrightarrow{k_2} D$$

A. (4 points) Write the equations for

$$\frac{d[C]}{dt} =$$

$$\frac{d[D]}{dt} =$$

in terms of [A], [B], [C], and [D] and k_1, k_{-1}, and k_2.

B. (6 points) Impose the steady-state approximation and solve for $[C]_{SS}$.

C. (4 points) Use the steady-state approximation to derive the rate law for $\frac{d[D]}{dt}$ in terms of [A], [B], and the rate coefficients k_1, k_{-1}, and k_2.

Blank page for calculations and extra space for your answers, should you need it.

D. (3 points) If $k_2[A]_0 \gg k_{-1}$, what are the apparent orders of the reaction with respect to [A] and [B]? Also, what is the effective rate coefficient (expressed in terms of k_1, k_{-1}, k_2, and $[A]_0$)?

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C$$

$$A + C \xrightarrow{k_2} D$$

E. (3 points) Same as part **D**, except for $k_2[A]_0 \ll k_{-1}$.

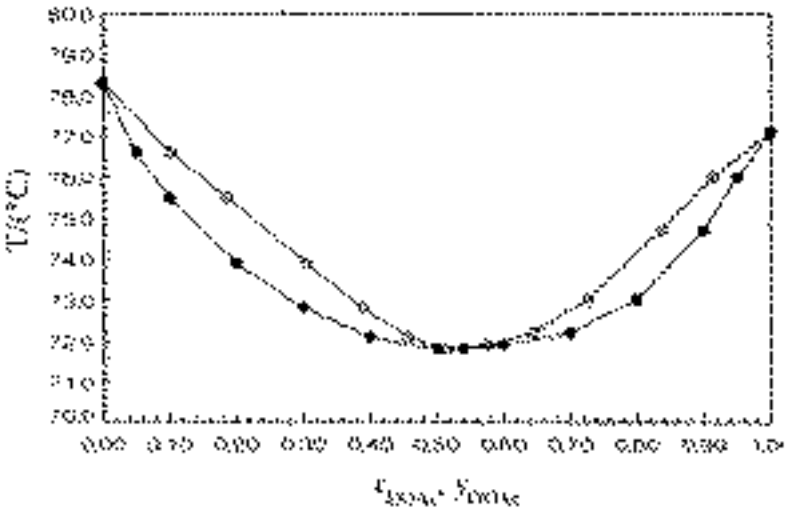
F. (6 points) Devise a strategy to determine each of the rate coefficients k_1, k_{-1}, and k_2 from
(*i*) rate measurements at large and small $[A]_0$ in combination with
(*ii*) tabulated values of ΔG_f° for A, B, and C.
Be as specific as possible. Write equations that show how the values of each of the rate coefficients could be determined.

G. (4 points) Suppose $[A]_0 = [B]_0 = 0$ but $[C]_0 \neq 0$. What would be the initial decay rate of [C]? What would be the final value of [D] (expressed in terms of $[C]_0$) assuming that C is completely consumed in the reaction?

Blank page for calculations and extra space for your answers, should you need it.

IV. Two-Component Phase Diagrams (30 + 3 extra credit points)

The (x,y) – T boiling point diagram for mixtures of ethanol (EtOH) and ethyl acetate (EtOAc) at p = 1.013 bar is shown below. The points (• and o) are from actual measurements.



A. (5 points) Label the regions of the diagram that correspond to liquid only (L), vapor only (V), and coexisting vapor and liquid (V + L) phases. Also label the boiling points (at p = 1.013 bar) of pure EtOH, T^*_{EtOH}, and EtOAc, T^*_{EtOAc}.

B. (4 points) Starting at T = 80°C and a single phase mixture of initially unknown composition (but known to contain more moles of EtOH than EtOAc), the temperature is lowered slowly until coexistence of liquid and vapor phases is first encountered at T = 75.0°C.

- Is this composition-Temperature point located on the dew point line or the bubble point line?
- What are the mole fractions of EtOAc in the vapor and liquid phases?
- Since, at T = 75.1°C this same mixture is entirely in a single phase, what is the mole fraction of EtOAc in the initially prepared mixture?

bubble or dew?

x_{EtOAc} =

y_{EtOAc} =

$$f_{EtOAc} = \frac{n_{EtOAc}}{n_{EtOAc} + n_{EtOH}} =$$

C. (3 points) For this same mixture of now known composition (f_{EtOAc}) [IF YOU WERE UNABLE TO DETERMINE A VALUE FOR f_{EtOAc} IN PART **B**, USE f_{EtOAc} = 0.30, (WHICH IS NOT THE CORRECT VALUE)], starting as a single phase at T = 70°C, the temperature is increased slowly until coexistence of liquid and vapor phases is first encountered.

- At what temperature does liquid/vapor phase coexistence first occur?
- What are the mole fractions of EtOAc in the liquid and vapor phases?

$T_{coexistence}$

x_{EtOAc}

y_{EtOAc}

D. (6 points, +3 extra credit pts.) Starting at the phase coexistence point in part **C**, the temperature of the mixture is increased in infinitesimal steps.

- In what direction do x_{EtOAc} and y_{EtOAc} change?
- If x_{EtOAc} decreases as T increases, why does it decrease?
- Does all of the liquid evaporate at some T before T = 78.3°C is reached?
- If so, give a qualitative reason.
- For 3 points extra credit, at what T does all of the liquid evaporate?

E. (8 points)

- Sketch an $(x,y) - p$ diagram that is both *qualitatively* correct and *qualitatively* consistent with EtOH, EtOAc (x,y) – T diagram shown at the beginning of this question.
- Label the V, L, and V + L regions.
- Identify the dew point and bubble point lines.
- Is p^*_{EtOAc} larger or smaller than p^*_{EtOH} ?
- Is an EtOH/EtOAc mixture an example of $2u_{AB} > u_{AA} + u_{BB}$ or $2u_{AB} < u_{AA} + u_{BB}$?

F. (4 points) An azeotropic mixture of EtOH and EtOAc boils at T = 71.8°C (p = 1.013 bar) and has composition $x_{EtOAc} = y_{EtOAc} = 0.54$.

- Starting with a single phase liquid at 70°C and $x_{EtOAc} = 0.20$, is it possible to design a fractional distillation procedure that yields pure EtOAc?
- Or, for the same mixture, is it possible to design a fractional distillation procedure that yields pure EtOH?

EtOAc? Why?

EtOH? Why?

Blank page for calculations and extra space for your answers, should you need it.