

Columbia University in the City of New York
New York, N.Y. 10027

Chemistry C2407x
Final Exam
December 22, 1998

Total Points: 300

1998
George Flynn
3 Hours

All questions are weighted equally. I have attempted to order the questions from the least difficult to the most difficult, but "beauty is in the eye of the beholder", so skip around to find the problems that are easiest for you. Good luck!

Please print your name in the boxes provided and sign where indicated. Tear off this sheet and pass it to the right for the proctors to pick up.

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Do not write anything else on this page. Answer the questions in the spaces provided on the following pages.

1a	1i	3b	5a	6d
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1b	1j	3c	5b	6e
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1c	2a	3d	5c
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1d	2b	4a	5d
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1e	2c	4b	5e
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1f	2d	4c	6a
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1g	2e	4d	6b
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1h	3a	4e	6c
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Problem 1: (50 Points)[Much in common with Oxtoby problems 3.42, 3.43, 3.44]For each of the following compounds, radicals, and ions, use the VSEPR model to deduce the bonding and structure. Give the steric number and the number of lone pairs. Indicate where all bond and lone pairs are located in the structure using a line for the bond pairs and two small circles for the lone pairs. You may find the electronic configuration of the following atoms useful.

O(At. Number = 8) $1s^2 2s^2 2p^4$

F(At. Number = 9) $1s^2 2s^2 2p^5$

P (At. Number = 15) $1s^2 2s^2 2p^6 3s^2 3p^3$

Cl (At. Number = 17) $1s^2 2s^2 2p^6 3s^2 3p^5$

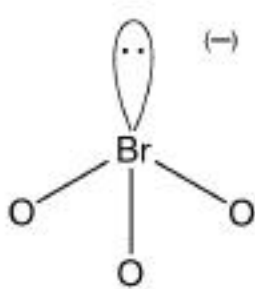
Br(At. Number = 35) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$

I(At. Number = 53) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^5$

Xe(At. Number = 54) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6$

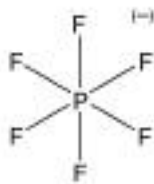
a) (5 points) BrO_3^- (Br is the central atom). Draw an appropriate structure, give the steric number and the number of lone pairs, and show all reasoning clearly.

Br has 7 valence electrons ($4s^2 4p^5$) plus one for minus charge. O requires 2 electrons per O atom to complete shell. Use 6 of 8 electrons to form 3 Br-O bonds with 2 left for lone pair. SN = 3 bonds + 1 lone pair = 4



b) (5 points) PF_6^- (P is the central atom). Draw an appropriate structure, give the steric number and the number of lone pairs, and show all reasoning clearly.

P has 5 valence electrons ($3s^2 3p^3$) plus one for minus charge. F requires 1 electrons per F atom to complete shell. Use 6 electrons to form 6 P-F bonds with 0 left for lone pair. SN = 6 bonds + 0 lone pair = 6

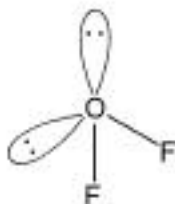


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c) (5 points) OF_2 (O is the central atom). Draw an appropriate structure, give the steric number and the number of lone pairs, and show all reasoning clearly.

O has 6 valence electrons ($2s^2 2p^4$). F requires 1 electron per F atom to complete shell. Use 2 of 6 electrons to form 2 O-F bonds with 4 left for lone pairs.

SN = 2 bonds + 2 lone pairs = 4

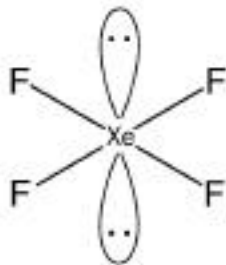


d) (5 points) XeF_4 (Xe is the central atom). Draw an appropriate structure, give the steric number and the number of lone pairs, and show all reasoning clearly.

Xe has 8 valence electrons ($5s^2 5p^6$). F requires 1 electron per F atom to complete shell. Use 4 of 8 electrons to form 4 Xe-F bonds with 4 left for 2 lone pairs.

SN = 4 bonds + 2 lone pairs = 6.

Octahedral structure with lone pairs in axial positions to be as separated as possible.

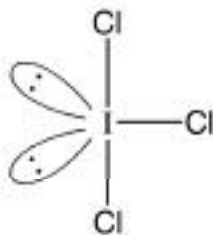


e) (5 points) ICl_3 (I is the central atom). Draw an appropriate structure, give the steric number and the number of lone pairs, and show all reasoning clearly.

I has 7 valence electrons ($5s^2 5p^5$). Cl requires 1 electron per Cl atom to complete shell.

Use 3 of 7 electrons to form 3 I-Cl bonds with 4 left for 2 lone pairs.

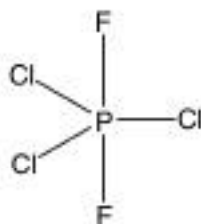
SN = 3 bonds + 2 lone pair = 5. Lone pairs always go in equatorial.



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f) (5 points) PCl_3F_2 (P is the central atom). Draw an appropriate structure, give the steric number and the number of lone pairs, and show all reasoning clearly.

P has 5 valence electrons ($3s^23p^3$). F and Cl require 1 electron per atom to complete shell. Use 5 electrons to form 2 P-F bonds and 3 P-Cl bonds with none left for lone pairs. $\text{SN} = 5 \text{ bonds} + 0 \text{ lone pair} = 5$. There are several isomeric structures but most stable is likely to be with Cl equatorial. Give full credit for all isomeric correct structures.

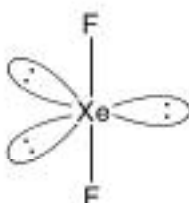


g) (5 points) XeF_2 (Xe is the central atom). Draw an appropriate structure, give the steric number and the number of lone pairs, and show all reasoning clearly.

Xe has 8 valence electrons ($5s^25p^6$). F requires 1 electron per F atom to complete shell. Use 2 of 8 electrons to form 2 Xe-F bonds with 6 left for 3 lone pairs.

$\text{SN} = 2 \text{ bonds} + 3 \text{ lone pairs} = 5$.

Lone pairs always go in equatorial for this structure.

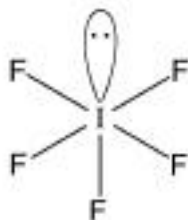


h) (5 points) IF_5 (I is the central atom). Draw an appropriate structure, give the steric number and the number of lone pairs, and show all reasoning clearly.

I has 7 valence electrons ($5s^25p^5$). F requires 1 electron per F atom to complete shell.

Use 5 of 7 electrons to form 5 I-F bonds with 2 left for 1 lone pair.

$\text{SN} = 5 \text{ bonds} + 1 \text{ lone pair} = 6$. Lone pair goes anywhere in this structure since all positions are equivalent.



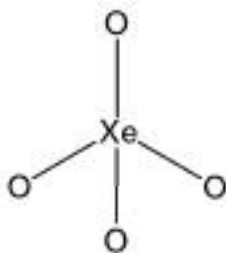
Print your name here:

i) (5 points) XeO_4 (Xe is the central atom). Draw an appropriate structure, give the steric number and the number of lone pairs, and show all reasoning clearly.

Xe has 8 valence electrons ($5s^2 5p^6$). O requires 2 electrons per O atom to complete shell.

Use 8 of 8 electrons to form 4 Xe-O bonds with 0 left for lone pairs.

SN = 4 bonds + 0 lone pairs = 4.

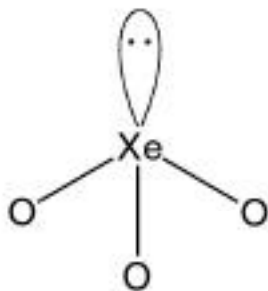


j) (5 points) XeO_3 (Xe is the central atom). Draw an appropriate structure, give the steric number and the number of lone pairs, and show all reasoning clearly.

Xe has 8 valence electrons ($5s^2 5p^6$). O requires 2 electrons per O atom to complete shell.

Use 6 of 8 electrons to form 3 Xe-O bonds with 2 left for 1 lone pair.

SN = 3 bonds + 1 lone pair = 4. All positions equivalent.



Print your name here:

Problem 2: (50 Points) [Much in common with Michaelis-Menten enzyme kinetics and unimolecular reaction models.]

Elementary termolecular reactions can be written as



with a rate law $d[P]/dt = k[A][B][C]$.

Many scientists have argued that a true termolecular reaction involving the simultaneous interaction (collision) of three species, especially at low pressures, is exceedingly unlikely. Anxious to win her first Nobel, our intrepid Columbia intensive general chemistry student Susie Student-Scientist (whose Mother's name was Sally Student and whose Father's name was Samy Scientist, in case you were wondering) has proposed the following kinetic scheme (all elementary steps) to explain how termolecular reactions *really* come about. Here k_i is the kinetic rate constant for the elementary reaction step indicated.



a) (10 Points) Write a differential rate equation for the rate of change of the intermediate species [AB] using Susie's kinetic scheme. Show all reasoning clearly.

$$d[AB]/dt = k_1 [A][B] - k_{-1} [AB] - k_2 [AB][C]$$

Print your name here:

b) (10 points) Making appropriate approximations solve the equation in part (a) above for [AB]. Show reasoning clearly! [Hint: How steady is your state?]

Steady state approximation:

$$d[AB]/dt = k_1[A][B] - k_{-1}[AB] - k_2[AB][C] = 0$$

$$k_{-1}[AB] + k_2[AB][C] = k_1[A][B]$$

$$[AB] \{k_{-1} + k_2[C]\} = k_1[A][B]$$

$$[AB] = k_1[A][B]/\{k_{-1} + k_2[C]\}$$

c) (10 points) Under what conditions would the result of part (b) above lead to a termolecular rate equation for the appearance of product, d[P]/dt? Show all work clearly!

$$d[P]/dt = k_2[AB][C]$$

$$\text{But from part (b), } [AB] = k_1[A][B]/\{k_{-1} + k_2[C]\}$$

$$\text{Therefore, } d[P]/dt = k_2[AB][C] = k_2[C] k_1[A][B]/\{k_{-1} + k_2[C]\}$$

$$d[P]/dt = k_2 k_1 [A][B][C]/\{k_{-1} + k_2[C]\}$$

$$\text{When } k_{-1} \gg k_2[C], k_{-1} + k_2[C] \approx k_{-1}$$

$$\text{Then, } d[P]/dt = k_2 k_1 [A][B][C]/\{k_{-1} + k_2[C]\} \approx k_2 k_1 [A][B][C]/k_{-1}$$

This is termolecular form.

Print your name here:

d) (10 points) Under what conditions would the result of part (b) above lead to a *bimolecular* (second order) rate equation for the appearance of product, $d[P]/dt$? Show all work clearly!

$$d[P]/dt = k_2[AB][C]$$

$$\text{But from part (b), } [AB] = k_1[A][B]/\{k_1 + k_2[C]\}$$

$$\text{Therefore, } d[P]/dt = k_2[AB][C] = k_2[C] k_1[A][B]/\{k_1 + k_2[C]\}$$

$$d[P]/dt = k_2 k_1 [A][B][C]/\{k_1 + k_2[C]\}$$

$$\text{When } k_1 \ll k_2[C], k_1 + k_2[C] \approx k_2[C]$$

$$\text{Then, } d[P]/dt = k_2 k_1 [A][B][C]/\{k_1 + k_2[C]\} \approx k_2 k_1 [A][B][C]/k_2[C]$$

$$d[P]/dt = k_2 k_1 [A][B][C]/k_2[C] = k_1 [A][B]$$

This is bimolecular form.

e) (10 points) Writing the rate of production of product

$$d[P]/dt = k[A][B][C],$$

as above, give the form of k based on your results for part (b). Tell what information you could obtain from a plot of $1/k$ versus $[C]$. Show all work clearly.

$$d[P]/dt = k_2[AB][C]$$

$$\text{But from part (b), } [AB] = k_1[A][B]/\{k_1 + k_2[C]\}$$

$$\text{Therefore, } d[P]/dt = k_2[AB][C] = k_2[C] k_1[A][B]/\{k_1 + k_2[C]\}$$

$$d[P]/dt = k_2 k_1 [A][B][C]/\{k_1 + k_2[C]\} = k[A][B][C]$$

$$k = k_2 k_1 / \{k_1 + k_2[C]\}$$

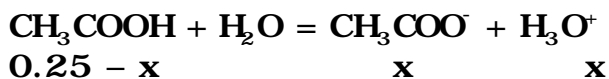
$$(1/k) = \{k_1 + k_2[C]\} / k_2 k_1 = \{k_1 / k_2 k_1\} + k_2[C] / k_2 k_1$$

Plot of $1/k$ vs $[C]$ has an intercept of $\{k_1 / k_2 k_1\}$ and a slope of $(1/k_1)$

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Problem 3: (50 Points) [Much in common with Oxtoby problems 10.45, 10.49, 10.54 and 10.55 and the titration recitation exercise.] A solution is prepared by adding 0.25 moles of acetic acid, CH_3COOH , to enough water to make precisely 1.00 liters of solution. The pH of the solution is found to be 2.68.

a) (10 points) Determine K_a , the acid ionization constant, for acetic acid. Show all reasoning and calculations clearly!



Here moles and concentration are the same since $V=1$ liter

$$K_a = [\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+] / [\text{CH}_3\text{COOH}]$$

$$K_a = (x)(x) / (.25 - x)$$

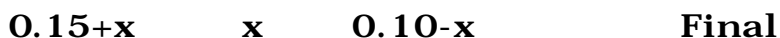
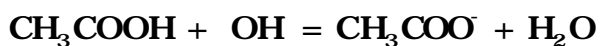
But $x = [\text{H}_3\text{O}^+] = 10^{-2.68}$ is given!

$$K_a = (10^{-2.68})(10^{-2.68}) / (.25 - 10^{-2.68})$$

$$K_a = (1.76) 10^{-5}$$

To this one liter of solution is added 0.100 moles of solid sodium hydroxide (NaOH), a strong base. The volume of the solution does not change.

b) (15 points) What is the pH of this new solution? Show all reasoning and calculations clearly!



Here moles and concentration are the same since $V=1$ liter

$$K_b = [\text{CH}_3\text{COOH}][\text{OH}^-] / [\text{CH}_3\text{COO}^-]$$

But this is a buffer with large concentration of weak acid

CH_3COOH and its conjugate base CH_3COO^- , so $x \ll 0.10$

$$K_b = (0.15+x)(x) / (.10-x) \approx (0.15)(x) / (.10)$$

$$x = K_b(0.10) / (0.15)$$

$$K_b = K_w / K_a$$

$$K_a = (1.76) 10^{-5} \text{ From part (a) and } K_w = 10^{-14}$$

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$$\text{So } K_b = K_w / K_a$$

$$K_b = 10^{-14} / (1.76) \cdot 10^{-5}$$

$$K_b = (5.68) \cdot 10^{-10}$$

$$x = K_b(0.10) / (0.15) = (5.68) \cdot 10^{-10} (0.10) / (0.15)$$

$$x = [\text{OH}] = (3.79) \cdot 10^{-10}$$

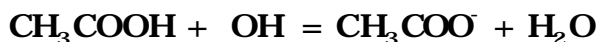
$$\text{pOH} = 9.42$$

$$\text{pH} = 14 - \text{pOH}$$

$$\text{pH} = 4.58$$

To this one liter of solution is added another 0.150 moles of solid sodium hydroxide (NaOH), a strong base. The volume of the solution still does not change.

c) (15 points) What is the pH of this new solution? Show all reasoning and calculations clearly!



$$0.15 \quad 0.15 \quad 0.10 \quad \text{Initial}$$

$$\approx 0 \quad \approx 0 \quad 0.25 \quad \text{Intermediate}$$

$$x \quad x \quad 0.25 - x \quad \text{Final}$$

Here moles and concentration are the same since $V=1$ liter

$$K_b = [\text{CH}_3\text{COOH}][\text{OH}^-] / [\text{CH}_3\text{COO}^-]$$

$$K_b = (x)(x) / (.25 - x) \approx (x)(x) / (.25)$$

$$x^2 = K_b(0.25)$$

$$\text{But from part (b) we have } K_b = (5.68) \cdot 10^{-10}$$

$$x = [\text{OH}] = (1.19) \cdot 10^{-5}$$

$$\text{pOH} = 4.92$$

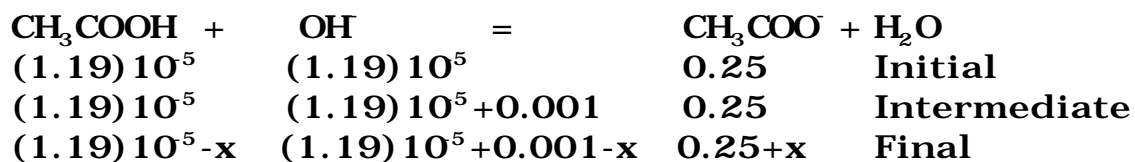
$$\text{pH} = 14 - \text{pOH}$$

$$\text{pH} = 9.08$$

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To this one liter of solution is added another 0.001 moles of solid sodium hydroxide (NaOH), a strong base. The volume of the solution still does not change.

d) (10 points) What is the pH of this new solution? Show all reasoning and calculations clearly!



Here moles and concentration are the same since $V=1$ liter
However, $x \ll 0.001$, so

$$0.001 \approx [\text{OH}^-]$$

$$\text{pOH} = 3.0$$

$$\text{pH} = 14 - \text{pOH}$$

$$\text{pH} = 11$$

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Problem 4: (50 Points) A gas mixture consists of (1/2) mole of Argon gas (At. Wt. = 40.0 gm/mole) and 1.0 mole of an unknown gas X. All you know about X is that it is either an atom (like Argon) or a diatomic molecule (like H₂). The initial volume of the sample is 10 liters and the initial temperature is 300° K. The gas is expanded to a final volume of 20 liters and a final temperature of 600° K by heating at constant pressure. A total of 9353.25 joules of heat (q) must be supplied to the sample to accomplish this expansion. You may assume that both Argon and X behave ideally.

i) **(10 points)** Determine the work, w, done by the gas mixture in this expansion. Show all reasoning clearly!

$$w = -\int_{V_i}^{V_f} p dV \quad p \text{ is constant}$$

$$w = -p \int_{V_i}^{V_f} dV = -p(V_f - V_i)$$

$$p = p_i = nRT_i/V_i$$

$$w = -nRT_i(V_f - V_i)/V_i$$

$$n = 1.5 \text{ moles, } T_i = 300, V_i = 10 \text{ liters, } V_f = 20 \text{ liters}$$

$$w = -(1.5)(8.314)(300)(20-10)/10 \text{ joules}$$

$$w = -450 R = -3741.3 \text{ joules}$$

j) **(5 points)** Determine the increase in kinetic energy for just the Argon gas in the sample. Show all reasoning clearly!

$$E = (3/2)nRT \text{ (K.E. of a monatomic ideal gas)}$$

$$\Delta E = (3/2)nR(T_f - T_i)$$

$$\Delta E = (3/2)(0.5)(8.314)(600-300) \text{ joules}$$

$$\Delta E = 1870.7 \text{ joules}$$

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k) (10 points) Based only on the information given so far, what is the increase in kinetic energy for **just** the unknown gas in the sample. (Be careful about your assumptions here. Remember X could be either an atom or a diatomic molecule.) Show all reasoning clearly.

$$\Delta E_{\text{tot}} = \Delta E(\text{Argon}) + \Delta E(\text{X})$$

$$\Delta E_{\text{tot}} = q + w$$

$$q = 9353.25 \text{ joules (given); } w = -3741.3 \text{ joules (part a)}$$

$$\Delta E_{\text{tot}} = 9353.25 + (-3741.3) \text{ joules} = 5612.0 \text{ joules}$$

$$5612.0 \text{ joules} = \Delta E(\text{Argon}) + \Delta E(\text{X})$$

$$\Delta E(\text{Argon}) = 1870.7 \text{ joules (part b)}$$

$$5612.0 \text{ joules} = 1870.7 \text{ joules} + \Delta E(\text{X})$$

$$\Delta E(\text{X}) = 3741.3 \text{ joules}$$

d) (10 points) How many degrees of freedom (translational plus rotational) does the unknown gas X have? Show all reasoning clearly.

$$\Delta E(\text{X}) = (N/2)nR(T_f - T_i)$$

$$N = \# \text{ of degrees of freedom of X}$$

$$\Delta E(\text{X}) = (N/2)(1.0)(8.314)(600-300) \text{ joules}$$

$$\Delta E(\text{X}) = N(1247.1 \text{ joules})$$

$$\Delta E(\text{X}) = 3741.3 \text{ joules (part c)}$$

$$N = (3741.3/1247.1) = 3.0$$

Print your name here:

A tiny hole is punched in the sample chamber, the gases escape, and their initial rate of effusion (escape) is measured. The unknown gas is found to escape 6.32 times faster than Argon.

e) (15 points) Give the formula weight (atomic or molecular weight as the case may be) of the unknown gas X. Show all reasoning clearly.

$$R_{\text{eff}} = (1/6)(N/V)C_{\text{rms}}A \text{ (Free Formulas)}$$

N = # of atoms, **V** = volume, **A** = area of hole, and

$$C_{\text{rms}} = [3RT/M]^{1/2}$$

$$R_{\text{eff}}(\text{X})/R_{\text{eff}}(\text{Argon}) = (N_{\text{X}}/N_{\text{Argon}})[C_{\text{rms}}(\text{X})/C_{\text{rms}}(\text{Argon})]$$

$$(N_{\text{X}}/N_{\text{Argon}}) = 1.0/0.5 = 2$$

$$[C_{\text{rms}}(\text{X})/C_{\text{rms}}(\text{Argon})] = [M_{\text{Argon}}/M_{\text{X}}]^{1/2} = [40.0/M_{\text{X}}]^{1/2}$$

$$R_{\text{eff}}(\text{X})/R_{\text{eff}}(\text{Argon}) = 6.32 \text{ (given)}$$

$$6.32 = (2) [40.0/M_{\text{X}}]^{1/2}$$

$$(3.16)^2 = 40.0/M_{\text{X}}$$

$$M_{\text{X}} = 4.00$$

Print your name here:

Problem 5: (50 points) The reaction of CO with O atoms is one of the most important chemical reactions in combustion. Suppose as a starting hypothesis that this reaction occurs via the following second order elementary reaction:



Although this is a second order reaction, most experimentalists working in real laboratory situations avoid like the plague such second order processes whenever they can. Instead they work in what is called the “pseudo first order regime”. Much of this problem is designed to help you understand what this means. The key to the “pseudo first order” picture for this combustion process is the realization that in any practical situation $[\text{CO}] \gg [\text{O}]$. Given this, the concentration of CO can be assumed to be **constant** throughout the reaction of CO with O to form CO_2 . Note, however, that $[\text{O}]$ is most definitely not constant!

a) (10 points) We begin with a simple observation. The rate constant k_1 for reaction (1) above increases by a factor of 5 when the temperature goes from 300 to 325° K. Determine the activation energy for reaction (1). Show all reasoning clearly.

$k = A \exp[-E_a/RT]$ (Free Formulas)

Simplest assumption, A independent of T

$$k(T_1)/k(T_2) = \exp[(-E_a/R)(1/T_1 - 1/T_2)]$$

$$k(T_1)/k(T_2) = 1/5 \quad (\text{Given})$$

$$k(T_1)/k(T_2) = 1/5 = \exp[(-E_a/R)(1/300 - 1/325)]$$

$$1/5 = \exp[(-E_a/R)(325-300)/(300)(325)]$$

$$\ln(1/5) = [(-E_a/R)(325-300)/(300)(325)]$$

$$-E_a/R = [(300)(325)/25] \ln(1/5)$$

$$E_a = [(300)(325)/25] R \ln(5)$$

$$E_a = [(12)(325)] (8.314 \text{ joules}) \ln(5)$$

$$E_a = 52,185.4 \text{ joules}$$

If use slightly more sophisticated, $A = \text{const}(T)^2$

$$k(T_1)/k(T_2) = [T_1/T_2]^{1/2} \exp[(-E_a/R)(1/T_1 - 1/T_2)]$$

$$-E_a/R = [(300)(325)/25] \ln[(1/5)(T_2/T_1)^{1/2}]$$

$$-E_a/R = [(300)(325)/25] \ln[(1/5)(325/300)^{1/2}]$$

$$E_a = [(12)(325)] (8.314 \text{ joules}) \ln[(5)(12/13)^{1/2}]$$

$$E_a = (32,424.6 \text{ joules}) \ln[(5)(12/13)^{1/2}]$$

$$E_a = 49,590.0 \text{ joules}$$

Print your name here:

b) (15 points) Write a differential rate law or equation for the disappearance of [O] and integrate this expression, using the assumption that $[CO] \gg [O]$, to find [O] as a function of time for reaction (1). Be sure to note and take advantage of the information given above about the behavior of CO when its concentration is large compared to that of O atoms. Show all reasoning clearly.

$$d[O]/dt = -k_1 [CO][O]$$

$$[CO] \gg [O], [CO] \approx \text{constant}$$

$$d[O]/[O] = -k_1 [CO] dt$$

$$\int d[O]/[O] = \int -k_1 [CO] dt$$

but, k_1 and [CO] are constant so

$$\int d[O]/[O] = -k_1 [CO] \int dt$$

$$\ln([O]) = -k_1 [CO] t + \text{const}$$

$$\text{At } t=0, [O] = [O]_0$$

$$\ln([O]_0) = -k_1 [CO](0) + \text{const}$$

$$\ln([O]_0) = \text{const}$$

$$\ln([O]) = -k_1 [CO] t + \ln([O]_0)$$

$$[O]/[O]_0 = e^{-k_1 [CO] t}$$

c) (10 points) If the initial concentration of CO in an experimental run is $[CO] = 0.100$ moles/liter and $k_1 = 10^4 \text{ sec}^{-1} \text{ M}^{-1}$ ($M =$ moles/liter), how long will it take for the initial concentration of O atoms, $[O]_0$, to fall to half its value under the conditions of part (b) above? Show reasoning clearly.

$$[O]/[O]_0 = e^{-k_1 [CO] t} \text{ (part b)}$$

$$t = t_{1/2} \text{ when } [O] = [O]_0/2$$

$$[O]/[O]_0 = 1/2$$

$$\ln(1/2) = -k_1 [CO] t_{1/2}$$

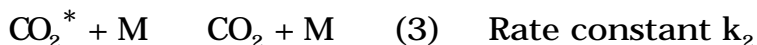
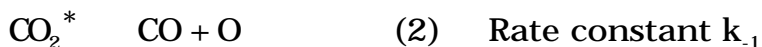
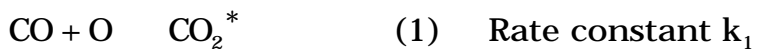
$$\ln(2)/k_1 [CO] = t_{1/2}$$

$$[(0.693)/(10^4)(0.100)] \text{ sec} = t_{1/2}$$

$$t_{1/2} = (6.93) 10^4 \text{ sec}$$

Print your name here:

An upstart young theorist, trying to make a scientific name for herself, has claimed that reaction (1) cannot possibly be a simple bimolecular encounter since the CO_2^* formed in (1) has sufficient energy to fall apart again to $\text{CO} + \text{O}$ resulting in the formation of no CO_2 . She proposes instead the kinetic scheme below, where all reactions written are elementary reaction processes:



Here CO_2^* is carbon dioxide with enough energy to fall apart and become $\text{CO} + \text{O}$ and M is an inert bath gas molecule (like N_2 or Argon) present in the same vessel as CO and O . CO_2 is stable carbon dioxide that lacks sufficient energy to fall apart to $\text{CO} + \text{O}$. Since M is inert, its concentration $[\text{M}]$ is constant in any experiment.

d) (5 points) Using the steady state approximation, determine $[\text{CO}_2^*]$ in terms of $[\text{CO}]$, $[\text{O}]$, and $[\text{M}]$. Show all reasoning clearly.

$$d[\text{CO}_2^*]/dt = k_1 [\text{CO}][\text{O}] - k_{-1} [\text{CO}_2^*] - k_2 [\text{CO}_2^*][\text{M}]$$

Steady State Approximation:

$$d[\text{CO}_2^*]/dt = k_1 [\text{CO}][\text{O}] - k_{-1} [\text{CO}_2^*] - k_2 [\text{CO}_2^*][\text{M}] = 0$$

$$k_1 [\text{CO}][\text{O}] - k_{-1} [\text{CO}_2^*] - k_2 [\text{CO}_2^*][\text{M}] = 0$$

$$k_1 [\text{CO}][\text{O}] = k_{-1} [\text{CO}_2^*] + k_2 [\text{CO}_2^*][\text{M}]$$

$$k_1 [\text{CO}][\text{O}] = \{k_{-1} + k_2 [\text{M}]\} [\text{CO}_2^*]$$

$$k_1 [\text{CO}][\text{O}] / \{k_{-1} + k_2 [\text{M}]\} = [\text{CO}_2^*]$$

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e) (10 points) Under what conditions does our intrepid theorist's model fit a kinetic expression where the production of CO_2 appears to be second order according to

$$d[\text{CO}_2]/dt = k[\text{CO}][\text{O}]$$

where k is some experimentally determined constant? Show all reasoning clearly.

$$d[\text{CO}_2]/dt = k_2[\text{CO}_2^*][\text{M}] \quad (\text{From equation 3})$$

$$\text{But, } k_1[\text{CO}][\text{O}]/\{k_1 + k_2[\text{M}]\} = [\text{CO}_2^*] \quad (\text{from part d}) \rightarrow$$

$$d[\text{CO}_2]/dt = k_2[\text{M}] k_1[\text{CO}][\text{O}]/\{k_1 + k_2[\text{M}]\}$$

$$\text{When } k_1 \ll k_2[\text{M}], \quad 1/\{k_1 + k_2[\text{M}]\} \approx 1/\{k_2[\text{M}]\}$$

$$d[\text{CO}_2]/dt = k_2[\text{M}] k_1[\text{CO}][\text{O}]/\{k_2[\text{M}]\}$$

$$d[\text{CO}_2]/dt = k_1[\text{CO}][\text{O}]$$

$$k = k_1$$

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Problem 6: (50 points) Water can be supercooled reversibly below its freezing point of 0° C to -10° C. Supercooled water can also be warmed reversibly from -10° C to 0° C. Once supercooled, however, a slight mechanical shock is sufficient to convert supercooled liquid water to solid ice **irreversibly** and **isothermally** at -10° C. The molar enthalpy of fusion for converting solid ice to liquid water at -10° C is 5649 joules/mole while the molar enthalpy of fusion for converting solid ice to liquid water at 0° C is 6025 joules/mole. The molar heat capacity of ice (constant pressure, independent of temperature) is 37.7 joules/mole-deg while the molar heat capacity of water (constant pressure, independent of temperature) is 75.3 joules/mole-deg. All of the following manipulations are carried out at a constant pressure of 1 atm.
a) (10 points) Calculate the entropy change when one mole of liquid water, initially at -10° C, is warmed reversibly to 0° C. Show all reasoning clearly.

$$\Delta S = \int dq_{\text{rev}}/T$$

$$dq_{\text{rev}} = C_p dT$$

$$\Delta S = \int (C_p/T) dT$$

C_p = constant pressure heat capacity of liquid water

C_p = constant independent of T (given)

$$\Delta S = C_p \int (dT/T)$$

$$\Delta S = C_p \ln(T_f/T_i)$$

C_p = 75.3 joules/mole-deg, T_f = 273, T_i = 263 (given)

$$\Delta S = [75.3 \text{ joules/mole-deg}] \ln(273/263)$$

$$\Delta S = [75.3 \text{ joules/mole-deg}] (3.73) 10^{-2}$$

$$\Delta S = 2.81 \text{ joules/mole-deg}$$

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b) (10 points) Calculate the entropy change when one mole of liquid water initially at 0° C is converted isothermally to ice at 0° C. (In case you have forgotten (!!), 0° C is the melting point of ice, defined to be the temperature at which water and ice are in equilibrium with each other.) Show all reasoning clearly.

$$\Delta S = \int dq_{\text{rev}}/T$$

Isothermal process, T = constant

$$\Delta S = (1/T) \int dq_{\text{rev}}$$

$$\Delta S = (q_{\text{rev}} / T)$$

Here $q_{\text{rev}} = -\Delta H_{\text{fusion}}$

T = 273 (Normal melting point of ice) (given)

$$\Delta H_{\text{fusion}} = 6025 \text{ joules/mole}$$

$$\Delta S = [-6025 \text{ joules/mole}] / 273 \text{ deg}$$

$$\Delta S = -22.07 \text{ joules/mole-deg}$$

c) (10 points) Calculate the entropy change when one mole of ice initially at 0° C is cooled reversibly to -10° C. Show all reasoning clearly.

$$\Delta S = \int dq_{\text{rev}}/T$$

$$dq_{\text{rev}} = C_p dT$$

$$\Delta S = \int (C_p/T) dT$$

C_p = constant pressure heat capacity of solid water (ice)

C_p = constant independent of T (given)

$$\Delta S = C_p \int (dT/T)$$

$$\Delta S = C_p \ln(T_f/T_i)$$

$C_p = 37.7 \text{ joules/mole-deg}$, $T_f = 263$, $T_i = 273$ (given)

$$\Delta S = [37.7 \text{ joules/mole-deg}] \ln(263/273)$$

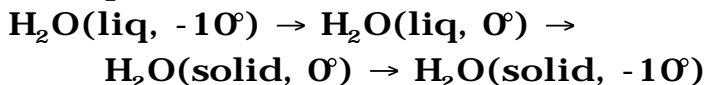
$$\Delta S = [37.7 \text{ joules/mole-deg}] (-3.73) 10^0$$

$$\Delta S = -1.41 \text{ joules/mole-deg}$$

Print your name here:

d) (10 points) Calculate the entropy change when one mole of liquid water at -10°C is converted isothermally and irreversibly to ice at -10°C . Show all reasoning clearly.

The irreversible path $\text{H}_2\text{O}(\text{liq}, -10^{\circ}) \rightarrow \text{H}_2\text{O}(\text{solid}, -10^{\circ})$ has the same initial and final states as the reversible path



Thus, these two paths must have the same ΔS since S is a state function.

ΔS for the reversible path is the sum of the three ΔS values calculated in parts (a), (b), and (c) above.

$$\Delta S = [2.81 + (-22.07) + (-1.41)] \text{ joules/mole-deg}$$

$$\Delta S = (-20.67) \text{ joules/mole-deg}$$

e) (10 points) Calculate the change in free energy (ΔG) when one mole of liquid water at -10°C is converted isothermally and irreversibly to ice at -10°C . Show all reasoning clearly.

$$\Delta G = \Delta H - T\Delta S$$

Isothermal process has $T = \text{constant}$, so

$$\Delta G = \Delta H - T\Delta S$$

$$T = 263, \Delta H_{\text{fusion}} = 5649 \text{ joules (given)}$$

$\Delta H = -5649 \text{ joules}$ (liquid to solid is opposite direction from fusion)

$$\Delta G = -5649 \text{ joules/mole} - (263 \text{ deg})(-20.67 \text{ joules/mole-deg})$$

$$\Delta G = -5649 \text{ joules/mole} + (5436 \text{ joules/mole})$$

$$\Delta G = -212 \text{ joules/mole}$$

The End