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Name Crazy Old Dude with 70 Cats

page   **1** (15) _____

2 (30) _____

3 (45) _____   _____
                            total (250)

4 (45) _____   ___
                            chk

5 (35) _____

6 (30) _____

7 (35) _____

8 (20) _____
                   Please write in this space.... *not*

1. (15 points) Summer is just around the corner. Let's make liquid nitrogen ice cream. Yum! (Well, we'll have to approximate ice cream as frozen water.) How many grams of liquid N_2 would be required to freeze 100 g of water, initially at 25.0 °C? Assume that the all the water ends up as ice at 0 °C. Also assume that the liquid nitrogen is at its boiling point, 77.3 K, and the cold gas formed when it vaporizes escapes immediately and is unable to provide any cooling. (Water's heat capacity is in the table provided. Water's enthalpy of fusion is 6.01 kJ/mol, and nitrogen's enthalpy of vaporization is 5.56 kJ/mol. Molecular weights are 18.0 g/mol for H_2O and 28.0 g/mol for N_2.)

N_2 $liq \rightarrow gas$ water ΔT water $\ell \rightarrow s$

$$m\left(5.56 \text{ kJ/mol}\right) = (100 \text{ g})\left(4.18 \tfrac{J}{g\cdot K}\right)(25 K) \; + \; (100 \text{ g})\left(\tfrac{1 \text{ mol}}{18 \text{ g}}\right)\left(6.01 \text{ kJ/mol}\right)$$

$$m\left(5.56 \text{ kJ/mol}\right) = 10.45 \text{ kJ} \quad + \quad 33.39 \text{ kJ}$$

$$m = 7.885 \text{ mol} \times \frac{28.0 \text{ g}}{1 \text{ mol}} = 221 \text{ g of liquid } N_2$$

/ 15

2. (18 points) The standard enthalpies of vaporization of 1-bromobutane, 1-chlorobutane, and 1-butanol are given below.

$$CH_3CH_2CH_2CH_2-\textbf{Br} \qquad CH_3CH_2CH_2CH_2-\textbf{Cl} \qquad CH_3CH_2CH_2CH_2-\textbf{OH}$$

$\Delta H°_{vap}$:   36.7   33.6   51 kJ/mol

(a) Explain briefly why the alcohol (the 3rd cmpd) has a much higher $\Delta H°_{vap}$ than the other two compounds.

5

−OH groups hydrogen bond − these interactions are stronger than the dipole-dipole interactions present in the others.

(b) Explain briefly why the first compound has a higher $\Delta H°_{vap}$ than the second.

4

Br is less electroneg than Cl, so it can't be greater dipole-dipole interactions.
Br is larger than Cl, thus more surface area + greater van der Waals interactions.

(c) The alcohol also has a higher entropy of vaporization ($S°_{vap}$ = 131 J/molK) than the other two compounds ($S°_{vap} \approx 97$ J/molK for each). Why?

4

Loss of hyd. bonding involves more loss of "order".

(d) The branched isomer of each compound, $(CH_3)_3C-\textbf{X}$ (X = Br, Cl, or OH), has $\Delta H°_{vap}$ about 5 kJ/mol *lower* than the "straight chain" isomers shown above. Why?

5

less surface area, so weaker van der Waals interactions (i.e. fewer H---H contacts are possible between molecules)

3. (12 points) When each compound below is dissolved in water, would the solution be acidic, basic, or neutral?
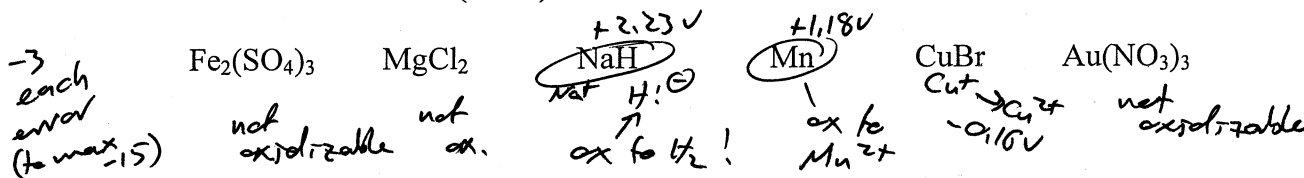
3 (a) $HOCH_2CH_2CH_2OH$ neutral

3 (b) $(CH_3)_2CHCO_2K$
$\{-CO_2^{\ominus} \ K^{\oplus}$ basic

3 (c) $(CH_3)_3NHBr$
$(CH_3)_3\overset{\oplus}{N}-H \ Br^{\ominus}$ acidic

3 (d) $NaNH_2$
$Na^+ \ .\overset{\ominus}{N}H_2 + H_2O \overset{\sim 100\%}{\longrightarrow} NH_3 + HO^-$ basic
strong base

/30

4. (15 points) Which of the following substances can reduce aqueous Cr^{3+} to chromium metal under standard conditions? (circle)

[handwritten margin: $\varepsilon° = -0.73V \rightarrow Cr$]

[handwritten left margin: -3 each error (to max -15)]

$Fe_2(SO_4)_3$ $\quad$ $MgCl_2$ $\quad$ NaH *(circled)* $\quad$ Mn *(circled)* $\quad$ CuBr $\quad$ $Au(NO_3)_3$

[handwritten annotations: +2.23 ✓ over NaH; +1.18v over Mn; not oxidizable; not ox.; NaF H⁻ ox to H₂! ; ox to Mn²⁺; Cu⁺→Cu²⁺ -0.16v; not oxidizable]

5. (30 points) Methylamine, CH_3NH_2, has $K_b = 4.40 \times 10^{-4}$. (a) Write the equilibrium that defines the K_b, showing all structures clearly.
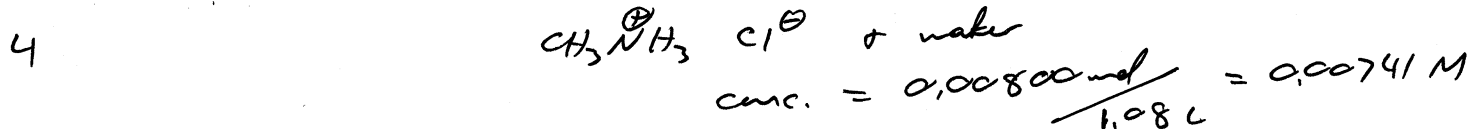
[handwritten left margin: 8]

[handwritten: curved arrows not required]

$$CH_3-\ddot{N}H_2 + H-\ddot{O}H \rightleftharpoons CH_3-\overset{\oplus}{N}H_3 + {}^{\ominus}\!:\!\ddot{O}H$$

$0.008\ M - x \qquad\qquad\qquad x \qquad\qquad x$
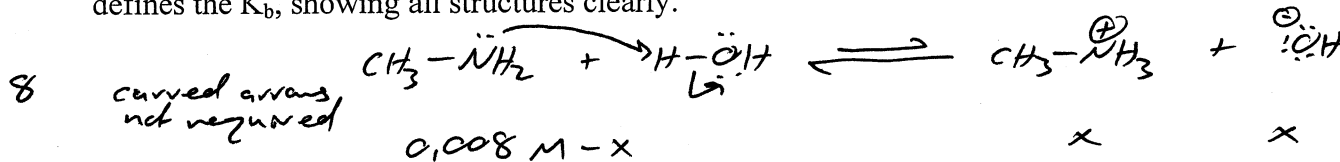
(b) Calculate the pH of a solution made by dissolving 0.00800 mol of methylamine in 1.00 L of water.

[handwritten left margin: 5]

$$4.40 \times 10^{-4} = \frac{x^2}{0.008 - x} \implies x = 0.0018\,76 \quad -\text{sig.nif. vxl to .008}$$

$$[HO^-] = 0.001\,67\ M$$

[handwritten: ↓ iterate 0.001641 ↓ again $x = 0.001673$ ok, that's it.]

$$pH = 11.2$$

(c) The solution from part b is titrated with 0.100 M hydrochloric acid. What volume of aq. HCl is required to reach the equivalence point?

[handwritten left margin: 3]

$$0.00800\ \text{mol} \times \frac{1\ L}{0.100\ \text{mol}} = 0.0800\ L = 80.0\ \text{ml}$$

(d) What are the major species present at the equivalence point, and what are their concentrations? Draw all structures clearly.

[handwritten left margin: 4]

$$CH_3\overset{\oplus}{N}H_3 \quad Cl^{\ominus} \quad + \text{ water}$$

$$conc. = \frac{0.00800\ \text{mol}}{1.08\ L} = 0.00741\ M$$

(e) What is the pH of the solution at the equivalence point?

[handwritten left margin: 5]

$$K_a = 2.27 \times 10^{-11} \qquad \text{consider } CH_3\overset{\oplus}{N}H_3 \text{ dissoc, as usual}$$

$$K_a = \frac{x^2}{0.00741 - x} \implies x = [H^+] = 4.104 \times 10^{-7}\ M$$

$$pH = 6.39 \qquad \left(\text{or, considering } [H^+] \text{ from } H_2O, \; 6.29\right)$$

(f) What was the pH of the solution when exactly half of the required amount of aq. HCl had been added?

[handwritten left margin: 5]

$$pH = pK_a$$

$$10.64$$

6. (13 points) You may have noticed the following trend within the K_b values listed in the table.

$$H_3C\text{–}\mathbf{NH_2} \qquad K_b = 4.4 \times 10^{-4}$$
$$H_2N\text{–}\mathbf{NH_2} \qquad K_b = 3.0 \times 10^{-6}$$
$$HO\text{–}\mathbf{NH_2} \qquad K_b = 1.1 \times 10^{-8}$$

(a) In the process that defines K_b, is the NH_2 group in these compounds protonated or deprotonated?   *protonated*
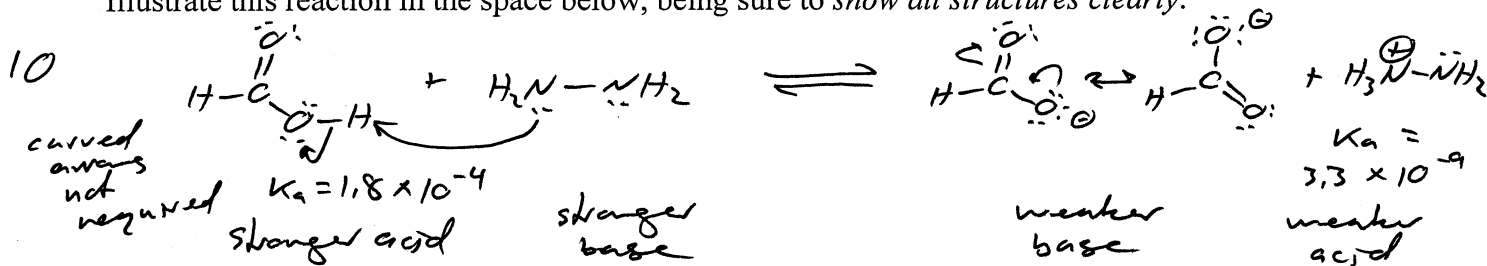
2

(b) Which compound above is the strongest base, and which is the weakest base?   *CH_3NH_2 is strongest, $HONH_2$ is weakest*

2

(c) Is K_b a thermodynamic or a kinetic parameter?   *thermodynamic !*

2

(d) Provide a brief *structural* explanation for the variation in K_b above.

7   *when –NH_2 group is protonated, the electronegative neighboring atom withdraws e^- density from the positive N, destabilizing the conj. acid. That is, making HO–$\overset{\oplus}{N}H_3$ is harder than making CH_3–$\overset{\oplus}{N}H_3$*

7. (32 points) (a) Hydrazine, NH_2NH_2, and formic acid, HCO_2H, undergo an acid-base reaction. Illustrate this reaction in the space below, being sure to *show all structures clearly*.

10

curved arrows not required $K_a = 1.8 \times 10^{-4}$ *stronger acid*   *stronger base*   *weaker base* $K_a = 3.3 \times 10^{-9}$ *weaker acid*

4 (b) Label the acids with their K_a values.

2 (c) Label the stronger acid and the weaker acid.

2 (d) Label the stronger base and the weaker base.

3 (e) Based on your stronger/weaker labels, which side of the reaction is favored at equilibrium?   *right*

3 (f) What is K_{eq} for the reaction?

$$K_{eq} = \frac{1.8 \times 10^{-4}}{3.3 \times 10^{-9}} = 5.4 \times 10^4$$

(g) What is $\Delta G°$ at 25 °C?

4

$$\Delta G° = -RT \ln K_{eq} = -27.0 \text{ kJ/mol}$$
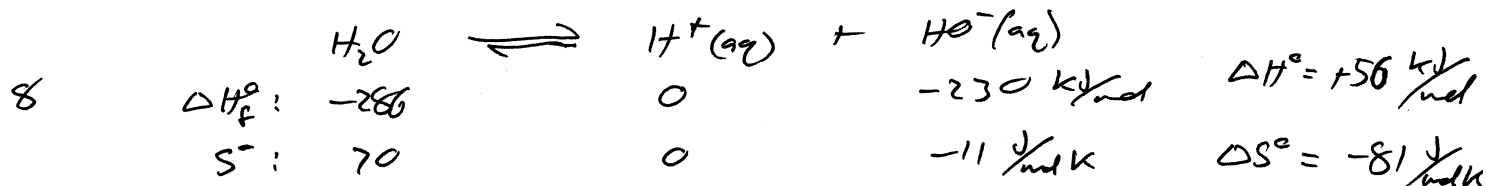
(h) Suggest two experimental methods by which one could determine the $\Delta H°$ for the reaction.

4   *measure K_{eq} vs Temp (plot $\ln K_{eq}$ vs $\frac{1}{T}$ ⟹ $\Delta H°$ from slope)*
measure $\Delta H°$ by calorimetry

page 4

45

8. (35 points) (a) Use the data in the tables provided to calculate $\Delta H°$ and $\Delta S°$ for the dissociation of liquid water to form aqueous H^+ and HO^-. Be sure to include units.

8

$$H_2O \rightleftharpoons H^+(aq) + HO^-(aq)$$

$\Delta H_f°:\quad -286 \qquad\qquad 0 \qquad\qquad -230\ kJ/mol \qquad \Delta H° = +56\ kJ/mol$

$S°:\quad\ \ 70 \qquad\qquad\ \ 0 \qquad\qquad -11\ J/mol\,K \qquad \Delta S° = -81\ J/mol\,K$

(b) Briefly explain the signs of $\Delta H°$ and $\Delta S°$ in terms of the chemical changes that take place.

5

dissociation involves loss of a bond + separation of charge, so $\Delta H°$ unfavorable.

negative $\Delta S°$ must come from an increase in solvent structure around the ions.

(c) What is $\Delta G°$ for this reaction at 25°C?

5

$$\Delta G° = \Delta H° - T\Delta S°$$
$$(56\ kJ/mol) - (298\,K)(-81\ J/mol\,K) = +80\ kJ/mol$$

watch the units!

(d) In the lab you measured the $\Delta H°$ for an exothermic reaction, and on the second midterm, you calculated the $\Delta H°$ for an endothermic reaction. Your $\Delta H°$ from part a was not zero, so this reaction is either exothermic or endothermic. So if you placed a sample of water in a coffee cup calorimeter, why would you not observe a change in temperature due to the reaction in part a?

3

rxn as written above is not spontaneous ($\Delta G°$ is pos), so nothing would happen to absorb heat.

(e) Based on your $\Delta G°$, what is K_{eq} at 25°C?

5

$$K_{eq} = e^{-\Delta G°/RT} = 9.48 \times 10^{-15}$$

$$= K_w$$

(f) Based on your K_{eq} (= "K_w") what is the pH of pure water at 25°C?

3

$$K_w = [H^+][HO^-] \qquad [H^+] = 9.74 \times 10^{-8} \Rightarrow$$

same

$$pH = 7.01$$

(g) Calculate the pH of pure water at 100°C.

6

assuming $\Delta H°$ & $\Delta S°$ are temp-independent

(or 7.0 to proper # sig figs)

$$\Delta G°\ \text{at}\ 373\,K = 86.2\ kJ/mol$$
$$\Downarrow$$
$$K_w = 9.04 \times 10^{-13}$$
$$\Downarrow$$
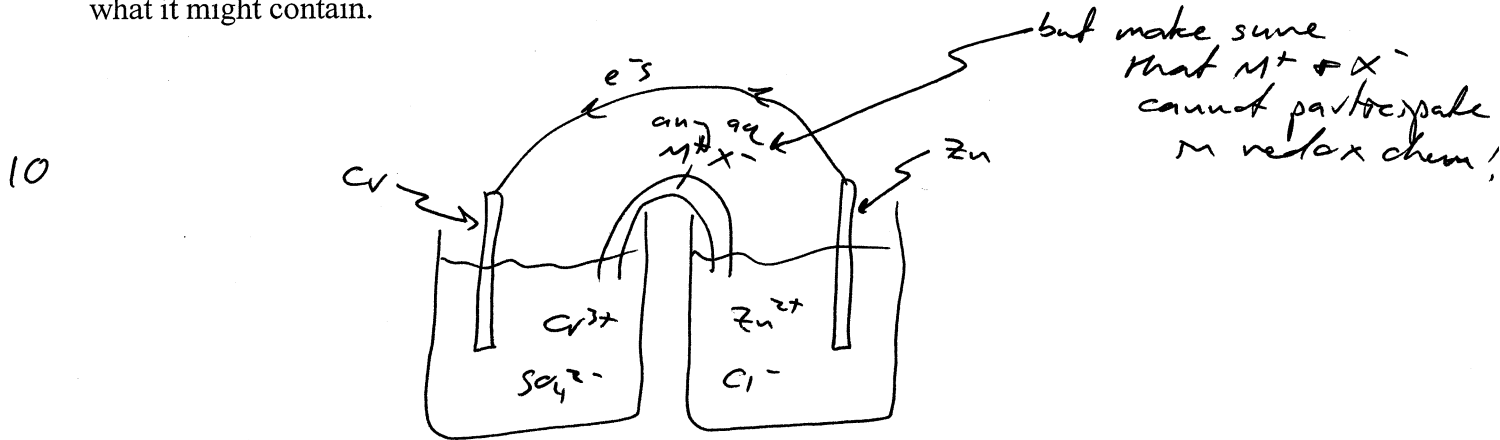$$pH = 6.02 \qquad \text{for neutral water at 100°C}$$

35

9. (30 points) An electrochemical cell is constructed with a zinc electrode and aqueous $ZnCl_2$ in one compartment and a chromium electrode and aqueous $Cr_2(SO_4)_3$ in the other. Both salts are very soluble in water.

(a) Write the balanced redox reaction. The sulfate and chloride ions do not participate in the redox chemistry and may be omitted.

5

$$2\,Cr^{3+} + 3\,Zn \rightleftharpoons 2\,Cr + 3\,Zn^{2+}$$

$-0.73\,V$

$+0.76\,V$

3

(b) What is the standard cell potential, $\varepsilon°$, for the reaction as you wrote it? $\varepsilon° = +0.03\,V$ ✓

(c) Sketch the electrochemical cell. Indicate the direction of electron flow under standard conditions, and label the anode and the cathode. If a salt bridge is required, show it and suggest what it might contain.

—but make sure that $M^+ \neq X^-$ cannot participate in redox chem!

10

e^-s · $M^+ X^-$ · Cr · Zn · Cr^{3+} · Zn^{2+} · SO_4^{2-} · Cl^-

(d) What is the cell potential when the concentration of $ZnCl_2$ is 0.90 M and the concentration of Cr^{3+} is 4.0×10^{-5} M? Which direction would the cell run?

6

$0.90\,M$

$4.0 \times 10^{-5}\,M$

$$\varepsilon = 0.03\,V - \frac{0.0257\,V}{6}\ln\left(\frac{[Zn^{2+}]^3}{[Cr^{3+}]^2}\right)$$

$$= -0.055\,V \quad \therefore \text{ cell would run "backward"}$$

$(-0.06\,V)$

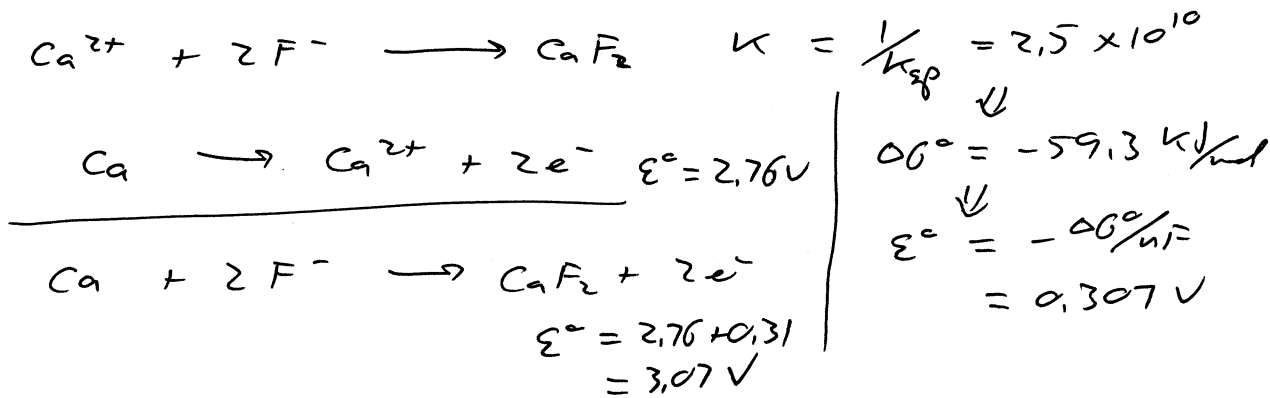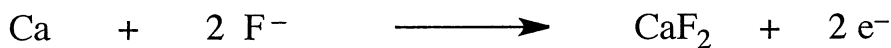(e) What is the equilibrium concentration of Cr^{3+} when $[Zn^{2+}] = 1.00$ M?

6

$$\varepsilon = 0, \text{ so } \varepsilon° = \frac{0.0257\,V}{6}\ln\left(\frac{(1\,M)^3}{[Cr^{3+}]^2}\right)$$
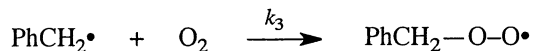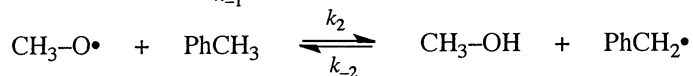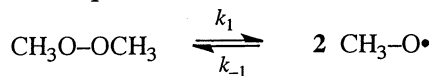
$0.03\,V$

$$[Cr^{3+}] = 0.030\,M$$

30

10. (17 points) Calcium fluoride is a very slightly water-soluble solid. Oxidation of calcium metal in the presence of fluoride ion produces CaF_2 directly, rather than aqueous Ca^{2+}. K_{sp} for CaF_2, is 4.0×10^{-11} at 25°C. Calculate the value of $\varepsilon°$ for the reaction below.

$$Ca \; + \; 2\,F^- \longrightarrow CaF_2 \; + \; 2\,e^-$$

$$Ca^{2+} + 2F^- \longrightarrow CaF_2 \qquad K = \frac{1}{K_{sp}} = 2.5 \times 10^{10}$$

$$Ca \longrightarrow Ca^{2+} + 2e^- \qquad \varepsilon° = 2.76V$$

$$\overline{\qquad\qquad\qquad\qquad\qquad\qquad}$$

$$Ca \; + \; 2F^- \longrightarrow CaF_2 + 2e^-$$

$$\varepsilon° = 2.76 + 0.31$$
$$= 3.07 \, V$$

$$\Delta G° = -59.3 \, kJ/mol$$

$$\varepsilon° = -\Delta G°/nF$$
$$= 0.307 \, V$$

11. (18 points) Many organic molecules undergo free radical-induced reactions with molecular oxygen, called autooxidation. Write the rate law for the autooxidation whose mechanism is shown below. Assume that the third step is rate-limiting, and use the *equilibrium approximation* to write an expression for the rate of formation of the major peroxide product, $PhCH_2OOH$, formed in the 4th step.

$$CH_3O{-}OCH_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,CH_3{-}O\bullet$$

$$CH_3{-}O\bullet \; + \; PhCH_3 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CH_3{-}OH \; + \; PhCH_2\bullet$$

$$PhCH_2\bullet \; + \; O_2 \overset{k_3}{\longrightarrow} PhCH_2{-}O{-}O\bullet$$

$$PhCH_2{-}O{-}O\bullet \; + \; PhCH_3 \overset{fast}{\longrightarrow} \mathbf{PhCH_2{-}OOH} \; + \; PhCH_2\bullet$$

$$2\,PhCH_2\bullet \overset{fast}{\longrightarrow} PhCH_2{-}CH_2Ph$$
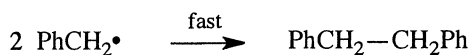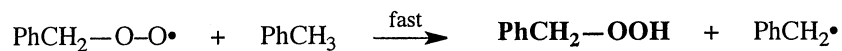
$$\frac{d[PhCH_2OOH]}{dt} = k_3 [O_2][PhCH_2\bullet]$$

$$[PhCH_2\bullet] = \frac{k_2 [CH_3O\bullet][PhCH_3]}{k_{-2}[CH_3OH]}$$

$$k_1[CH_3OOCH_3] = k_{-1}[CH_3O\bullet]^2$$

$$[CH_3O\bullet] = \sqrt{\frac{k_1[CH_3OOCH_3]}{k_{-1}}}$$

$$\frac{d[PhCH_2OOH]}{dt} = \frac{k_1^{1/2} k_2 k_3 [O_2][PhCH_3][CH_3OOCH_3]^{1/2}}{k_{-1}^{1/2} k_{-2}[CH_3OH]}$$

35

12. (20 points) Recall that the activation energy for rotation around a C=C π-bond is 270 kJ/mol. As a consequence, alkenes, which contain the C=C unit, can exist in geometrically distinct "stereoisomeric" forms that do not interconvert at ordinary temperatures, as shown below for 2-butene, $CH_3-CH=CH-CH_3$.
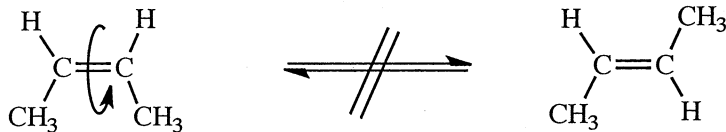
Organic compounds that contain one or more silicon atoms in place of carbon are expected to have unusual properties that could potentially lead to new materials. The E_a for rotation around the **Si=C** π-bond is 165 kJ/mol, and the E_a for rotation around the **Si=Si** π-bond is about 95 kJ/mol.

(a) Calculate the rate constant and the timescale for rotation around a Si=C π-bond at 100 °C. Assume an Arrhenius A-factor of $10^{13.2}$ sec^{-1}.

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$$k = 10^{13.2} e^{-Ea/RT} \leftarrow 373k \quad \text{watch the units !}$$

$$k = 1.238 \times 10^{-10} \text{sec}^{-1} \quad \tau = 1/k = 8.08 \times 10^{9} \text{sec}$$

$$= 266 \text{ years}$$

(b) Repeat part a for rotation around an Si=Si π-bond at 25 °C.

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$$k = 10^{13.2} e^{-Ea/RT} \leftarrow 298k$$

$$k = 3.53 \times 10^{-4} \text{sec}^{-1} \Rightarrow \tau = 2840 \text{sec}$$

$$= 47 \text{ min}$$

(c) If you prepared two separate samples of the stereoisomeric forms of $CH_3-SiH=SiH-CH_3$ (analogous to the structures drawn above), at what temperature (in °C) would you need to store them to ensure no more than 1% interconversion within a year?

10

$$\ln\left(\frac{[x]_0}{[x]}\right) = kt$$

$\nearrow \frac{1}{0.99}$ $\nearrow$ 1 yr = 3.156×10^{7} sec $\Rightarrow k = 3.185 \times 10^{-10} \text{sec}^{-1}$

$$k = A e^{-Ea/RT}$$

$$3.185 \times 10^{-10} \text{sec}^{-1} = (10^{13.2} \text{sec}^{-1}) e^{-(95000 \text{ J/mol})/(8.314 \text{ J/mol·k}) T}$$

$$T = 218.6 \text{ k} = -54.4 \text{ °C}$$

need a freezer at or below −55 °C ! Brrrr...

20