

Aug 79.5

1/6 <sup>or</sup> 90% or higher  
100%

Chemistry 12

Fall, 2008

Examination II

Please answer all six questions. Your reasoning should be clearly and concisely indicated.

$$pH = pK_a + \log \frac{\text{base}}{\text{acid}}$$

Useful Information:

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

$$\Delta G = -n\mathcal{F}\mathcal{E}$$

$$\Delta G^0 = -RT \ln K$$

$$\mathcal{E} = \mathcal{E}^0 - (RT/n\mathcal{F}) \ln Q$$

$$pH = -\log_{10} [H^+]$$

$$R = 8.3145 \text{ J/mol K}$$

$$\mathcal{F} = 96485 \text{ C/mol}$$

Emma Fink

Name

Amrabb Bonney 2pm

Discussion Instructor & Time

1	16
2	33.5 + 2 (36)
3	15
4	3
5	15
6	15
$\Sigma$	97.5 + 2 = 99.5

Bonney ←

1) For each of these statements, state whether it is TRUE or FALSE.

a.  $\Delta G^\circ$  is independent of temperature.

False ✓  
 $\Delta G^\circ = -RT \ln K$  thus  $\Delta G^\circ$  depends on temperature.

b. Gibbs Free energy is a state function.

True ✓  $\Delta G = \Delta H - T\Delta S$  Entropy and enthalpy are both state functions, thus  $\Delta G$  is a state function.

c. For an isothermal process,  $\Delta H$  must be zero.

False ✓ Even in an isothermal process  $q$  does not have to = 0. Under constant atmospheric pressure no PV work conditions, this would mean that  $\Delta H$  isn't necessarily 0.

d. The second law of thermodynamics requires that the entropy change associated with any chemical reaction be positive.

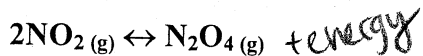
False ✓  $\Delta S_{\text{sys}}$

16 / 16

The second law of thermodynamics states that  $\Delta S_{\text{univ}} \geq 0$ , where  $\Delta S_{\text{univ}} = 0$  in a reversible process. While a process can be reversible, however, as long as  $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} > 0$ ,  $\Delta S_{\text{sys}}$  may decrease. Thus, as long as  $\Delta S_{\text{univ}} \text{ overall} > 0$ ,  $\Delta S_{\text{sys}}$  may be  $< 0$  and this statement is false. good.

33's  
36

2)  $\text{NO}_2$  is a reddish-brown gas that is one of the most prominent air pollutants and a poison when inhaled.  $\text{N}_2\text{O}_4$  gas is a powerful oxidizing agent, is colorless, highly toxic, corrosive, and famous for its use as a rocket propellant. These two gases exist in equilibrium according to the reaction



At 298 K, the equilibrium lies to the right (with  $\text{N}_2\text{O}_4$  predominating), while at higher temperatures (above 330 K),  $\text{NO}_2$  is the major species present at equilibrium. For the process described here, state whether the thermodynamic quantities listed are equal to zero, greater than zero, less than zero or cannot be decided, using the symbols =0, >0, <0 or ? respectively at 298 K. Please provide the reasoning you used to arrive at your answer.

4 a.  $\Delta G^\circ < 0$   
If the equilibrium lies to the right  $K > 1$ . Since  
 $\Delta G^\circ = -RT \ln K$ , if  $K > 1$ ,  $\Delta G^\circ < 0$ .

4 b.  $\Delta H^\circ < 0$   
Since at low temps the equilibrium lies to the right but at high temps the equilibrium lies to the left,  
 $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$   $\Delta H^\circ < 0$ . At low temps, the contribution of  $-T\Delta S^\circ$  is minimal, so a negative  $\Delta H^\circ$  can make  $\Delta G^\circ < 0$ .

4 c.  $\Delta S^\circ < 0$   
Since at high temps,  $K < 1$  (the equilibrium lies to the left) and  $\Delta G^\circ > 0$ ,  $\Delta S^\circ$  must be negative. At high temps, the term  $-T\Delta S^\circ$  will be positive and will overcome  $\Delta H^\circ$ .

4 d. At 350 K for this reaction, is  $\Delta G^\circ = 0, >0, <0$  or ? Explain your answer.  
 $\Delta G^\circ > 0$  ✓ At this temperature, the equilibrium lies to the left. By  $\Delta G^\circ = -RT \ln K$ , when  $K < 1$   
 $\Delta G^\circ > 0$ .

Not adiabatic

normaler can be exchanged volume constant vacuum

A pure sample of  $\text{NO}_2$  at 298 K is placed into a sealed, rigid and evacuated flask. It is observed to react to form  $\text{N}_2\text{O}_4$  predominantly. During this process, the temperature of the flask is observed to increase and then return to room temperature. For the isothermal reaction  $2\text{NO}_2(\text{g}) \leftrightarrow \text{N}_2\text{O}_4(\text{g})$  at 298 K under these conditions, provide the algebraic signs for the following quantities, stating your reasons: (You may assume that both  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  behave as ideal gases.)

For:

$PV = nRT$

4

e.  $q < 0$  Since when the reaction is conducted neither adiabatically nor isothermally, the temperature is observed to increase, this would suggest that  $q < 0$ . While for many cases with ideal gases

$\Delta E = 0$  when conducted isothermally, there is a chemical rxn occurring here so this point is no longer necessarily valid.

4

f.  $w = 0$  The flask is evacuated so it is not pushing against any  $P_{\text{ext}}$  as it expands to fill the flask. Once it has expanded to fill the flask, no volume change can occur as the flask is rigid, so  $-P\Delta V = 0$

4 I talked my way into getting some of my pants back but I wouldn't recommend it.

g.  $\Delta H < 0$   $\Delta PV = \Delta P V$  no volume change  $w = 0$   $q < 0$  thus  $\Delta E < 0$

Since  $\Delta H = \Delta E + \Delta PV$

and  $\Delta E$  is  $< 0$  ( $q < 0, w = 0$ ) and  $V$  is constant

$\Delta E + \Delta PV = \Delta H$

$\Delta PV < 0$  from the ideal gas equation,  $\Delta H < 0$   $\Delta PV = \Delta(RTn)$

$\Delta E - RT = \Delta H$

$V\Delta P = TR\Delta n$

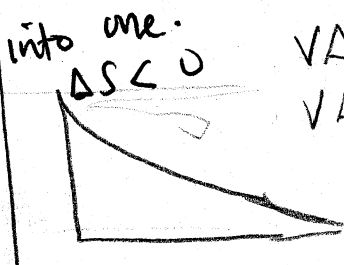
$V\Delta P = RT(-1)$

$-RT < 0$

$\uparrow$  always  $+ \text{const}$

h.  $\Delta S$  We do not know how much we do not know if it's at equilibrium.

$\Delta S_{\text{system}} = q_{\text{rev}}$  Two gaseous molecules change into one.  $\Delta G = \Delta H - T\Delta S$



We do not know the  $q_{\text{rev}}$  of this process, hence we do not know  $\Delta S_{\text{sys}}$ . The sign of  $\Delta G$  doesn't help us since  $\Delta H$  is negative

$\Delta S_{\text{surr}} = \frac{-q}{T}$   $q < 0$  thus  $\Delta S_{\text{surr}} > 0$

$\Delta G = \Delta G^\circ - RT \ln Q$

$\Delta S_{\text{univ}} > 0$

h) However, the fact that 1 mol of gas is being formed from 2 mol of gas would suggest that  $\Delta S < 0$  as does the fact that  $q < 0$ . We however, do not know  $q_{\text{rev}}$  we do not know how long it takes

3)

a. Calculate the pH of a 0.200 M solution of HOAc (acetic acid).  $K_a$  of the acid =  $1.85 \times 10^{-5}$

$$K_a = \frac{[H^+][OAc^-]}{[HOAc]}$$

$$1.85 \times 10^{-5} = \frac{(x)(x)}{(0.2 - x)}$$

(Assume  $x \ll 10^{-7}$ )  
assumption valid  
 $pH = -\log[H^+] = -\log(0.0019143105)$

$pH = 2.717987596 \approx 2.718$

alternatively we could have assumed  $x \ll 0.2$

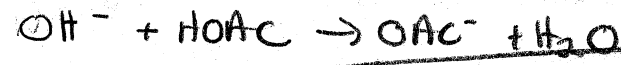
$$3.7 \times 10^{-6} - 1.85 \times 10^{-5} x = x^2$$

$$x = 0.0019143106 = H^+$$

$$x = -0.0019328106 \leftarrow \text{reject bec negative}$$

b. Calculate the volume of 0.10 M NaOH solution that must be added to 500.0 ml of 0.200 M HOAc to give a solution that has pH = 3.0.

add 0.131639006 mol NaOH to 1 mol HOAc



pH = 3 thus  $-\log[H^+] = 3$

$V \approx 0.182 \text{ L NaOH added}$

$0.185 = \frac{.1V}{.1 - .1V}$   
 $.00185 = .00185V$   
 $.00185 = .10185V$   
 $0.10181639006 = V$

$\log[H^+] = -3 \quad [H^+] = 10^{-3}$

$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right)$   
 $3 = -\log(1.85 \times 10^{-5}) + \log X$

$-1.732828272 = \log y$   
 $0.185 = x = \frac{\text{mol base}}{\text{mol acid}}$  (volumes cancel)

$0.00181639006 \text{ mol NaOH}$

Calculate the volume of 0.10 M NaOH solution that must be added to 500.0 ml of 0.200 M HCl to give a solution that has pH = 3.0

pH = 3  $[H^+] = 10^{-3}$

thus  $[HCl] = 10^{-3}$   
better addition, not dissociation

$(.1) V = x$   
 $\frac{\text{moles}}{\text{liter}} = M$

$\frac{0.1 \text{ mol HCl} - 0.1V \text{ mol NaOH}}{500/1000 + V} = 10^{-3}$

$0.1 - 0.1V \text{ NaOH} = 5 \times 10^{-4} + 10^{-3}V$

$1.485148515 \leftarrow \text{Total V}$

$0.1 - 5 \times 10^{-4} = 10^{-3}V + 0.1V$

$\frac{.0995}{.101} = \frac{.101V}{.101}$

$.9851485149 = V \approx .985 \text{ L added}$

5

4)

The cell potential (E) depends on concentrations. The Nernst equation, which expresses this dependence, is given on the cover page.

Consider a concentration cell containing 0.20 M solutions of  $\text{AgNO}_3$  in both compartments. For this cell, what is the value of  $\ln Q$ ,  $E^\circ$ , and E? (Explain your answers)

$E^\circ = 0$  For a concentration cell,  $E^\circ$  always = 0.

When reactants and products are all at 1M concentrations, there is no difference in concentration to lead to a voltage.  
or: when at equilibrium  $K=1$  thus  $E^\circ = \frac{RT}{nF} \ln K$   $E^\circ = 0$  ✓

$E = 0$

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

$$E = -\frac{RT}{nF} \ln \frac{.2M}{.2M}$$

$$E = -\frac{RT}{nF} \ln 1$$

$$E = 0$$

Since the concentrations in both compartments are equal,  $\ln Q = 0$ . Thus  $E = 0$ .  $Q = 1$  ✓

$$\ln Q = 0$$

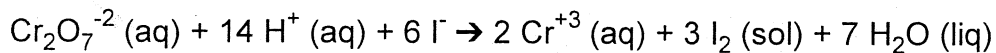
$$\ln Q = \ln \frac{\text{prod}}{\text{reactants}} = \ln \frac{.2M}{.2M} = \ln 1 = 0$$

$Q = \frac{[\text{products}]}{[\text{reactants}]}$  in this cell, the products and reactants are the same species at the same concentration (and rxn)

$$\text{thus } Q = 1$$

$$\ln Q \text{ thus } = 0$$

5) An electrochemical cell is built around the overall reaction



298K

The standard reduction potential for dichromate ion to chromium (III) ion is 1.33 V and the standard reduction potential of solid iodine to iodide ion is 0.54 V.

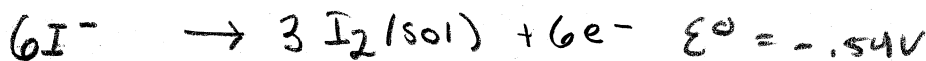
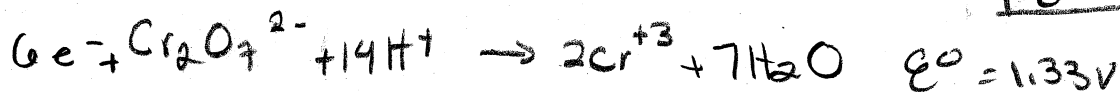
a) Calculate the standard voltage of this cell.

~~reduction~~ dichromate to chromium (III) ion  $E^\circ = 1.33 \text{V}$   
~~oxidation~~ iodide ion to solid iodine  $E^\circ = -0.54 \text{V}$

6e-  
6e-

or

$$E^\circ = 0.79 \text{V}$$



$$E^\circ = 0.79 \text{V}$$

b) Calculate the equilibrium constant of the overall reaction.

$$\Delta G^\circ = -nFE^\circ$$

$$\Delta G^\circ = -RT \ln K$$

$$\frac{nFE^\circ}{nF} = \frac{RT \ln K}{nF}$$

$$E^\circ = \frac{RT \ln K}{nF}$$

$$0.79 \text{V} = \frac{(8.3145 \text{ J/Kmol})(298 \text{K}) \ln K}{(6)(96485 \text{ C/mol})}$$

$$+184.5804073 = \ln K$$

$$1.453042818 \times 10^{80} \approx 1.45 \times 10^{80} = K$$

- c) At pH=0, with  $[Cr_2O_7^{2-}] = 1.5 \text{ M}$  and  $[I^-] = 0.40 \text{ M}$ , the measured voltage is 0.87 V. Find the concentration of  $[Cr^{+3}]$  in the cell.

pH=0  $\frac{-\log[H^+]}{10} = 0$   
 $[H^+] = 1 \text{ M}$

$$E = E^0 - \frac{RT}{nF} \ln Q$$

$$.87 = .79 \text{ V} - \frac{(8.3145 \text{ J/mol}\cdot\text{K})(298 \text{ K})}{(6)(96485 \text{ C/mol})} \ln \frac{[Cr^{+3}]^2}{(1.5 \text{ M})^6 (0.4 \text{ M})^{14} (1)^4}$$

$$.08 = - .0042799762 \ln Q$$

$$-18.69169289 = \ln \frac{[Cr^{+3}]^2}{(1.5 \text{ M})(0.4 \text{ M})^6}$$

$$7.626072334 \times 10^{-9} = \frac{[Cr^{+3}]^2}{(1.5 \text{ M})(0.4 \text{ M})^6}$$

$$4.68545884 \times 10^{-11} = [Cr^{+3}]^2$$

$$6.845041156 \times 10^{-6} \text{ M} = [Cr^{+3}] \approx 6.85 \times 10^{-6} \text{ M}$$

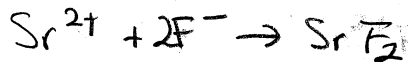
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6) 40.0 mL of 0.0800 M  $\text{Sr}(\text{NO}_3)_2$  and 80.0 mL of 0.0500 KF are mixed, producing a precipitate of strontium fluoride, whose  $K_{sp}$  is  $2.8\text{E}-9$ . Find the concentrations of strontium ion and fluoride ion remaining in solution.

$$K_{sp} = [\text{Sr}^{2+}][\text{F}^-]^2$$

$$2.8 \times 10^{-9} = [\text{Sr}^{2+}][\text{F}^-]^2$$



but  $K_{sp}$  refers to

$$2.8 \times 10^{-9} = \left( \frac{.0032 - x}{.12} \right) \left( \frac{.004 - 2x}{.12} \right)^2 \quad \text{SrF}_2 \rightarrow \text{Sr}^{2+} + 2\text{F}^-$$

.12 from  
120 mL

1000 mL / L

Start with .0032 mol  $\text{Sr}(\text{NO}_3)_2$

.004 mol KF

$$2.8 \times 10^{-9} = \frac{(.0032 - x)(.004 - 2x)(.004 - 2x)}{.001728}$$

$$4.8384 \times 10^{-12} = (.0032 - x)(1.6 \times 10^{-5} - .008x - .008x + 4x^2)$$

$$4.8384 \times 10^{-12} = (.0032 - x)(1.6 \times 10^{-5} - .016x + 4x^2)$$

$$0 = 5.12 \times 10^{-8} - 5.12 \times 10^{-5}x + .0128x^2 - 1.6 \times 10^{-5}x + .016x^2 - 4x^3 - 4.8384 \times 10^{-12}$$

the correct root ←

$$x = .0019686577$$

$$y = .0020321835$$

$$z = .0031991588$$

Since  $2x$  must be less than

.004 (we can't have

$$[\text{Sr}^{2+}] = \frac{.0032 - .0019686577}{.12}$$

$$= .0102611858 \text{ M}$$

$$\approx .010 \text{ M}$$

that wasn't added in the first place these two roots are rejected.

$$[\text{F}^-] = \frac{.004 - 2(.0019686577)}{.12}$$

$$= 5.223716667 \times 10^{-4} \text{ M}$$

$$\approx 5.2 \times 10^{-4} \text{ M}$$