

This exam is 7 pages (4 pieces of paper double sided). Make sure you have all pages. The first two pages contain useful information. Constants on the front and a periodic table on the back. You can tear this page off for convenience. The exam itself starts on page 2. Pages 2+3 contain 10 multiple-choice questions. Each page thereafter contains problems that require brief explanation and/or calculation.

Some potentially useful constants: $K_w @ 25^\circ\text{C}$ 1.00×10^{-14} , $R = 8.314 \text{ J}/(\text{mol K})$ or $0.0821 \text{ (L atm)}/(\text{mol K})$ $c = 2.99 \times 10^8 \text{ m/s}$ $h = 6.626 \times 10^{-34} \text{ J s}$, Avagadro's number $= 6.023 \times 10^{23}$, $\pi = 3.14159$, $e = 2.7183$, density of water 1.00 g/mL .

<u>Acid</u>	<u>K_a</u>	<u>Salts</u>	<u>K_{sp}</u>
Hydrofluoric (HF).....	6.8×10^{-4}	Silver chloride (AgCl).....	1.8×10^{-10}
Carbonic (H_2CO_3).....	4.5×10^{-7}	Silver bromide (AgBr).....	5.0×10^{-13}
Hydrocyanic (HCN).....	6.2×10^{-10}	Magnesium carbonate (MgCO_3).....	3.5×10^{-8}
Formic (HCOOH).....	1.8×10^{-4}		
Fe^{3+}	6×10^{-3}		
Al^{3+}	1×10^{-5}		

<u>Base</u>	<u>K_b</u>
Ammonia (NH_3)	1.76×10^{-5}

<u>molecule</u>	<u>$\Delta S^\circ_f \text{ J}/(\text{mol K})$</u>
$\text{SO}_2(\text{g})$	248.4
$\text{O}_2(\text{g})$	205.0
$\text{SO}_3(\text{g})$	256.3

Point breakdown:

MC	20 (2ea)
11	4
12	4
13	12 (a:7, b:5)
14	14 (a:8, b:6)
15	24 (a:6, b:5, c:5, d:8)
16	<u>22 (a:8, b:6, c:4, d:4)</u>
	100 total

6) What happens to the pH of a carbonic acid (H_2CO_3) solution as you add magnesium nitrate ($\text{Mg}(\text{NO}_3)_2$)?

- (A) The pH goes up (B) The pH goes down
(C) The pH does not change

7) Which solution has the greatest buffer capacity?

- (A) A solution 0.1M in HF and 0.005 M in NaF.
(B) A solution 0.1M in HF and 0.05 M in NaF.
(C) A solution 0.001M in HF and 0.0005 M in NaF.
(D) A solution 0.01M in HF and 0.500 M in NaF.

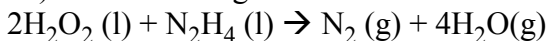
8) Which of the following has the highest molar entropy?

- (A) Glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) (B) Sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$)
(A) Ribose ($\text{C}_5\text{H}_{10}\text{O}_5$)

9) If you do 6.25 kJ of work on a system that absorbs 0.32 kJ of heat from the surroundings, what is the change in internal energy of the system?

- (A) 6.25 kJ (B) 0.32 kJ (C) 6.57 kJ (D) 5.93 kJ

10) What is the sign of ΔS° for the following reaction?



- (A) Positive (B) Negative (C) Zero

Problems: (80pts. Total) Work all problems in the space provided.

11) What are the pH and pOH of a 0.035M HCl aqueous solution at 25°C?

$$\text{pH} = -\log 0.035$$

$$\text{pH} = 1.46$$

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

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

$$\text{pOH} = 12.54$$

12) What are the $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ in an aqueous solution at 25°C with $\text{pOH} = 5.56$?

$$[\text{OH}^-] = 10^{-\text{pOH}}$$

$$[\text{OH}^-] = 10^{-5.56}$$

$$[\text{OH}^-] = 2.75 \times 10^{-6}$$

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

$$[\text{H}_3\text{O}^+] = K_w / [\text{OH}^-]$$

$$[\text{H}_3\text{O}^+] = 1.00 \times 10^{-14} / 2.75 \times 10^{-6}$$

$$[\text{H}_3\text{O}^+] = 3.63 \times 10^{-9}$$

13) The weak acid HA has a K_a of 2.39×10^{-5} :

a) What is the pH of a 0.15M solution of HA?

$$\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^- \quad K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = 2.39 \times 10^{-5}$$

$$x^2 = 2.39 \times 10^{-5} (0.15\text{M})$$

$$x = 1.89 \times 10^{-3}$$

$$\text{pH} = -\log 1.89 \times 10^{-3}$$

$$\text{pH} = 2.72$$

b) What is the K_b of A^- ?

$$K_w = K_a K_b$$

$$K_b = K_w / K_a$$

$$K_b = 1.00 \times 10^{-14} / 2.39 \times 10^{-5}$$

$$K_b = 4.18 \times 10^{-10}$$

14) Suppose that you have 250mL of a solution that has a $[Cl^-]$ of $2.5 \times 10^{-7} M$.

a) How many moles of $AgNO_3(s)$ must be added until $AgCl(s)$ begins to precipitate?



Ppt starts when $Q_{sp} = K_{sp}$

$$[x][2.5 \times 10^{-7}] = 1.8 \times 10^{-10}$$

$$x = 7.2 \times 10^{-4} M$$

moles = MV

$$\text{moles} = 7.2 \times 10^{-4} M \times .250 L = 1.8 \times 10^{-4} \text{ moles}$$

b) This type of a titration (yes, it is still a titration even though there are no acids and bases) could be used to determine an unknown Cl^- ion concentration in drinking water. Suppose that $AgBr(s)$ is indistinguishable from $AgCl(s)$. How would the presence of a large concentration of Br^- ions ($[Br^-] > [Cl^-]$) in your unknown sample effect your experimentally determined Cl^- concentration (too high, too low, not at all)? Explain.

$AgBr$ ($K_{sp} = 5.0 \times 10^{-13}$) is less soluble than $AgCl$ ($K_{sp} = 1.8 \times 10^{-10}$) so Br^- ions would cause $AgBr$ to ppt. before $AgCl$. The amount of $AgNO_3(s)$ needed to get to the ppt. would be less than the amount for Cl^- alone. $K_{sp} = [Ag^+][Cl^-]$ and therefore the experimentally determined Cl^- ion concentration would be $[Cl^-] = K_{sp}/[Ag^+]$. K_{sp} is a constant and $[Ag^+]$ is too low making $[Cl^-]$ too high.

15) In the titration of 50mL of 0.010M formic acid with 0.100M sodium hydroxide:

a) How much NaOH is needed to reach the equivalence point?

$0.010M \times 0.050L = 0.0005 \text{ mole formic acid} = \text{mole NaOH needed for equivalence pt.}$

$0.10M \times x = 0.0005 \text{ mole}$

$x = 0.005L = 5mL$

b) Is the solution acidic or basic at the equivalence point? Explain (do not calculate).

At the equivalence point there is no more formic acid so the pH is that of the formate ion alone. This ion is a base so the solution is basic.

c) What is the pH at the midpoint?

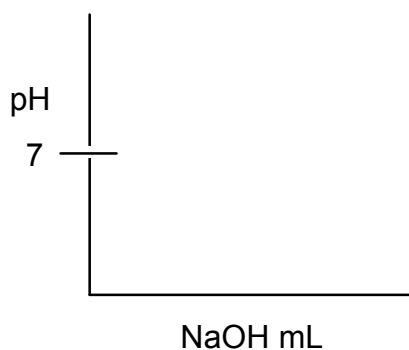
At the midpoint $pH = pK_a$

Formic acid $K_a = 1.8 \times 10^{-4}$

$pK_a = -\log 1.8 \times 10^{-4}$

$pH = pK_a = 3.74$

d) Sketch the titration curve labeling the equivalence point and midpoint at the proper pH as determined above.



16) a) What is $\Delta S_{\text{rxn}}^{\circ}$ for the reaction $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$

$$\Delta S_{\text{rxn}}^{\circ} = \sum m \Delta S_{\text{prod}}^{\circ} - \sum n \Delta S_{\text{react}}^{\circ}$$

$$\Delta S_{\text{rxn}}^{\circ} = [2(256.3 \text{ J/mol K})] - [2(248.4 \text{ J/mol K}) + 205.0 \text{ J/mol K}]$$

$$\Delta S_{\text{rxn}}^{\circ} = -189.2 \text{ J/mol K}$$

b) If $\Delta H_{\text{rxn}}^{\circ}$ is -197.8 kJ/mol , what is ΔS_{surr} if the reaction takes place at 298 K and constant pressure?

$$\Delta S_{\text{surr}} = -\Delta H_{\text{rxn}}^{\circ} / T$$

$$\Delta S_{\text{surr}} = -(-197800 \text{ J/mol}) / 298 \text{ K}$$

$$\Delta S_{\text{surr}} = 663 \text{ J/mol K}$$

c) Is the reaction spontaneous? Explain.

$$\Delta S_{\text{univ}} = \Delta S_{\text{surr}} + \Delta S_{\text{sys}}$$

$$\Delta S_{\text{univ}} = 663 \text{ J/mol K} - 189.2 \text{ J/mol K}$$

$$\Delta S_{\text{univ}} = 475 \text{ J/mol K}$$

Yes, the reaction is spontaneous because $\Delta S_{\text{univ}} > 0$

d) What happens as the temperature is increased?

As the temperature is increased, $\Delta H_{\text{rxn}}^{\circ} / T$ becomes smaller and so the positive ΔS_{surr} term above becomes smaller until eventually, ΔS_{sys} dominates and $\Delta S_{\text{univ}} < 0$. The reaction becomes non-spontaneous.

Alternatively from a Le Chatellier's principle point of view, the reaction is exothermic so when you put heat in (raise T) the reaction shifts in the direction that absorbs heat (to the left)