1) The equilibrium constant K_c for forming Nitrogen monoxide gas from its elements is 1.0×10^{-5} at 1500K. If 0.80 mol of N_2 and 0.20 mol of O_2 were placed in a 1L flask, what is the equilibrium concentration of NO?

A) 6.32×10^{-4} M
[✓ B)] 1.26×10^{-3} M
C) 3.16×10^{-4} M
D) 8.94×10^{-4} M
E) 1.79×10^{-3} M

$N_2 + O_2 \longrightarrow 2NO \qquad K_c = 1\times10^{-5}$

I	0.8M	0.2M	0
C	−x	−x	+2x
E	0.8	0.2	2x

$\frac{0.8}{1\times10^{-5}} >> 400$ ✓

$$1\times10^{-5} = \frac{(2x)^2}{(0.8)(0.2)}$$

$$(1\times10^{-5})(0.8)(0.2) = 4x^2$$

$$\sqrt{\frac{(1\times10^{-5})(0.8)(0.2)}{4}} = x$$

$$6.32\times10^{-4} = x$$

$$[NO] = 2x = 1.26\times10^{-3} M$$

2) K_c for the reaction $C_2 + D_2 \leftrightarrow 2CD$ is 2.0 at 600°C. 0.50 mol of each reactant are put in a 2L flask, predict the percent yield of CD at 600°C.

$\frac{0.5 mol}{2 l} = 0.25M$

$C_2 + D_2 \rightarrow 2CD \qquad K_c = 2$

I	0.25	0.25	0
C	−x	−x	+2x
E	0.25−x	0.25−x	2x

$\frac{0.25}{2} < 400$

$$2 = \frac{(2x)^2}{(0.25-x)(0.25-x)}$$

$$\sqrt{2 = \frac{(2x)^2}{(0.25-x)^2}}$$

$$\sqrt{2} = \frac{2x}{0.25-x}$$

$$0.25\sqrt{2} - x\sqrt{2} = 2x$$

$$0.25\sqrt{2} = 2x + x\sqrt{2}$$

$$0.25\sqrt{2} = x(2+\sqrt{2})$$

$$x = \frac{0.25\sqrt{2}}{2+\sqrt{2}}$$

$$x = 0.1036\ M$$

actual yield $= 2x = 0.2071\ M$

theoretical yield $= (0.25M)(2) = 0.5\ M$

$$\%\ \text{yield} = \frac{0.2071}{0.5} \times 100\% = \boxed{41.4\%}$$

3) For which of the following reactions does $K_c = K_p$ at 25°C?

I: $3\ A(s) + 5\ B(g) \rightleftharpoons 3\ AB(g) + B_2\ (g)$, $\Delta H = 30$ J $\quad \Delta n = 4-8=-4$

II: $2\ C(g) + 2\ D(g) \rightleftharpoons 4\ CD(g)$, $\Delta H = -15$ J $\quad \Delta n = 4-4=0$

III: $2\ Y(s) + E_2Y(g) \rightleftharpoons YE(g) + Y_2(g) + E(g)$, $\Delta H = 0$ J $\quad \Delta n = 3-1=2$

A) I only [✓ B) II only] C) III only D) I and II only E) II and III only

$$K_p = K_c(RT)^{\Delta n}$$

Δn: change in moles of gas

$K_p = K_c$ when $\Delta n = 0$

4) Sodium-24 is a radioactive isotope that decays via first order kinetics and has a half-life of 15 hours. What fraction of an original sample of sodium-24 will decompose in 3 days?

$$t_{1/2} = \frac{\ln(2)}{K} \qquad K = \frac{\ln(2)}{t_{1/2}} = \frac{\ln(2)}{15\text{hr}} = 0.0462\ \text{hr}^{-1}$$

$(3\ \text{days})(24\ \text{hr/day}) = 72\ \text{hr}$

$$\ln[A]_t = -Kt + \ln[A]_0$$

$$\ln[A]_t - \ln[A]_0 = -Kt$$

$$\ln\frac{[A]_t}{[A]_o} = -Kt$$

$$\frac{[A]_t}{[A]_o} = e^{-Kt} = e^{-(0.0462\,hr^{-1})(72\,hr)}$$

$$\frac{[A]_t}{[A]_o} = 0.0359 = 3.59\% \text{ is left}$$

$$100\% - 3.59\% = \boxed{96.41\%} \text{ has decomposed}$$

5) Given the overall reaction $2H_2 + 2NO \rightarrow 2H_2O + N_2$ and the following mechanism:

Step 1: $NO + NO \rightleftharpoons N_2O_2$ (fast)

Step 2: $N_2O_2 + H_2 \rightarrow H_2O + N_2O$ (slow)

Step 3: $N_2O + H_2 \rightarrow N_2 + H_2O$ (fast)

$$\text{rate} = K[N_2O_2][H_2]$$

$$[N_2O_2] = [NO]^2$$

$$\text{rate} = K[NO]^2[H_2]$$

Which of the following is/are true?

~~I~~: The rate law for the overall reaction is Rate = $k[N_2O_2][H_2]$

~~II: The~~ absolute value of the rate of change of H_2 is ½ the rate of change of N_2

~~III~~: The rate of the reaction is dependent only on H_2

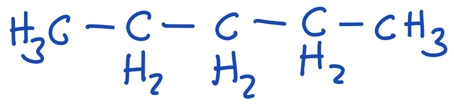
A) Only I B) Only II C) II and III D) I and II [✓ E) None]

$$\text{rate} = -\frac{1}{2}\frac{\Delta[H_2]}{\Delta t} = -\frac{1}{2}\frac{\Delta[NO]}{\Delta t} = \frac{1}{2}\frac{\Delta[H_2O]}{\Delta t} = \frac{\Delta[N_2]}{\Delta t}$$

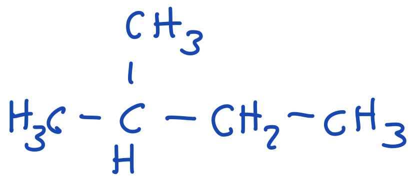
$$-\frac{1}{2}\frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[N_2]}{\Delta t}$$

$$-\frac{\Delta[H_2]}{\Delta t} = 2\frac{\Delta[N_2]}{\Delta t}$$

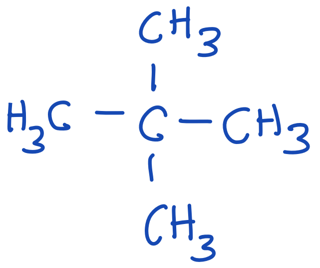
6) Draw all the structural isomers of C_5H_{12}.



$H_3C-\underset{H_2}{C}-\underset{H_2}{C}-\underset{H_2}{C}-CH_3$



$H_3C-\overset{CH_3}{\underset{H}{C}}-CH_2-CH_3$



$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$

7) Given the reaction for the following hypothetical weak acid: HA+ $H_2O \rightleftharpoons$ NaA + H_3O^+, which would increase the buffer component concentration ratio?

I: Adding 0.1 M NaOH to the buffer   II: Adding 0.1 M HCl to the buffer

[✓ A) I only]   B) II only   C) both   D) none

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

8) Calculate the pH of a 0.20 M Na_2CO_3 solution. K_a of HCO_3^- is $4.8x10^{-11}$

A) 8.49
B) 2.19
C) 5.51
[✓ D) 11.81]
E) 9.62

$$HCO_3^- + H_2O \rightleftharpoons \underset{\substack{\downarrow \\ \text{C.B. of } HCO_3^-}}{CO_3^{2-}} + H_3O^+ \quad K_a = 4.8\times10^{-11}$$

$$K_b[CO_3^{2-}] = \frac{10^{-14}}{4.8\times10^{-11}} = 2.08\times10^{-4}$$

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^- \quad K_b = 2.08\times10^{-4}$$

$\frac{0.2}{K_b} > 400$

I	0.2	X	0	0
C	$-x$		$+x$	$+x$
E	~0.2		x	x

$$2.08\times10^{-4} = \frac{x^2}{0.2}$$

$$x = \sqrt{(2.08\times10^{-4})(0.2)}$$

$$x = 0.00645 = [OH^-]$$

$$pOH = -\log(0.00645) = 2.19 \Rightarrow pH = 11.81$$

9) A 1.00g piece of chalk containing $CaCO_3$ (and other materials) was placed in 500. mL of hydrochloric acid solution with an initial pH of 1.00. After all of the $CaCO_3$ reacts with the HCl (forming CO_2 gas, H_2O, Ca^{2+}, and Cl^-), the final pH is 1.19. About what mass percent of the chalk was $CaCO_3$?

$$CaCO_3 + 2HCl \rightleftharpoons CO_2 + H_2O + Ca^{2+} + 2Cl^-$$

	CO_3^{2-}	$+2H^+ \rightleftharpoons$	CO_2	$+ H_2O$
I	?	0.1	0	
C	$-x$	$-2x$	$+x$	
E	0	0.0646	x	

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

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

$[H^+]_i = 10^{-1} = 0.1\ M$

$[H^+]_f = 10^{-1.19}$

$= 0.0646M$

$0.1 - 2x = 0.0646$

$x = 0.0177\ M$

$[CO_3^{2-}]_0 - 0.0177\ M = 0$

$[CO_3^{2-}]_0 = 0.0177\ M$

$\frac{0.0177 mol\ CO_3^{2-}}{L} \cdot 0.5L = 0.00885\ mol\ CO_3^{2-}$

$\downarrow$

$0.00885\ mol\ CaCO_3$

$(0.00885\ mol\ CaCO_3)(100g/mol) = 0.885g\ CaCO_3$

$\frac{0.885g}{1.00g} \times 100\% = \boxed{88.5\%}$

10) Hypobromous acid is a commonly used disinfectant in swimming pools. At 25°C HBrO dissociates in water with a $K_a = 2.3\times10^{-9}$. Is this dissociation a spontaneous process when $[H_3O^+] = 6.0\times10^{-4}$ M, $[BrO^-]$ = 0.10 M, and [HBrO] = 0.20 M?

$$HBrO + H_2O \rightleftharpoons BrO^- + H_3O^+$$

A) Yes, because $\Delta G > 0$

[✓ B) No, because $\Delta G > 0$]

C) Yes, because $\Delta G < 0$

D) No, because $\Delta G < 0$

$$Q = \frac{(6\times10^{-4})(0.1)}{0.2} = 3\times10^{-4}$$

$$\Delta G = RT\ln\frac{Q}{K} = (8.314J/mol\cdot K)(298K)\cdot\ln\frac{3\times10^{-4}}{2.3\times10^{-9}}$$

$\Delta G = 29{,}182\ J/mol$

11) What is the value for the standard free energy of the following reaction: ΔG°

$Pb(s)\ |\ Pb^{2+}(aq)\ ||\ Mg^{2+}(aq)\ |\ Mg(s)$

[✓ A) +432.3 kJ/mol] B) −432.3 kJ/mol C) +216.1 kJ/mol D) −216.1 kJ/mol

Anode (ox.): $Pb \rightarrow Pb^{2+} + 2e^- \quad E^\circ = -0.13$

Cathode (red): $Mg^{2+} + 2e^- \rightarrow Mg \quad E^\circ = -2.37\ V$

$$E^\circ_{cell} = -2.37V - (-0.13V) = -2.24V = -2.24\ J/C$$

$$\Delta G^\circ = -nFE^\circ_{cell}$$

$$\Delta G^\circ = -(2\ mol\ e^-)(96{,}500\ C/mol)(-2.24\ J/C)$$

$$\Delta G^\circ = 432{,}320J = 432.32\ KJ$$

12) A hydrogen fuel cell operates with the following half reactions:

Anode: $H_{2(g)} \rightarrow 2H^+ + 2e^-$
Cathode: $O_{2(g)} + 4e^- + 4H^+ \rightarrow 2H_2O_{(l)}$

If the initial P_{O2} is 4 atm, what initial P_{H2} is required for the cell to generate a voltage of 1.25V?

Anode: $2H_2 \rightarrow 4H^+ + 4e^- \quad E^\circ = 0\ V \qquad E_{cell} = 1.25$

Cathode: $O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \quad E^\circ = 1.23\ V$

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O(l) \quad E^\circ_{cell} = 1.23\ V$$

$$E_{cell} = E^\circ_{cell} - \frac{0.0592}{n}\log Q \qquad Q = \frac{1}{P_{H_2}^2 \cdot P_{O_2}}$$

$$1.25 = 1.23 - \frac{0.0592}{4}\log Q \qquad 0.0447 = \frac{1}{P_{H_2}^2 \cdot 4}$$

$$0.02 = -0.0148\log Q \qquad 0.179 = \frac{1}{P_{H_2}^2}$$

$$-1.35 = \log Q$$

$$Q = 0.0447$$

$$\boxed{P_{H_2} = 2.37\ atm}$$

13) The magnetic moment of an inorganic complex represents the number of unpaired electrons present in its d-orbital splitting configuration. A complex $[MCl_6]^{4-}$ has a magnetic moment of around 3. Which two elements in the 3d block could be "M"?

A) V and Ni [✓ B) V and Co] C) Sc and Ni D) Sc and Co

3 unpaired e^-

$[MCl_6]^{4-}$

+2 −6

M^{2+}

↑ ↑ ↑ __ __

3d

↓

M

↑↓ ↑ ↑ ↑ __ __

4s 3d

M = V

OR

M^{2+}

↑↓ ↑↓ ↑ ↑ ↑

3d

M

↑↓ ↑↓ ↑↓ ↑ ↑ ↑

4s 3d

M = Co

14) Rank the following in order of increasing magnetism. I: $[Mn(NO_2)_6]^{1-}$ II: $[Fe(en)_3]^{2+}$ III: $[CoCl_3F_3]^{3-}$

A) I < II < III B) I < III < II C) II < III < I [✓ D) II < I < III] E) III < I < II

I) Mn^{5+} 3d

__ __

↑ ↑ ↑ 3 unpaired

II) Fe^{2+} 6d

__ __

↑↓ ↑↓ ↑↓ strong field ligand

0 unpaired

III) Co^{3+} 6d

↑ ↑

↑↓ ↑ ↑ 4 unpaired

15) What is the binding energy per nucleon of fluorine?

$$(18.998\,\text{amu})(1.66\times10^{-27}\,\text{g/amu}) = 3.1547\times10^{-26}\,\text{Kg}$$

$$\Delta m = (\overset{\substack{\#\text{protons}\\\downarrow}}{9})(\overset{\substack{m_p\\\downarrow}}{1.67262192\times10^{-27}}) + (\overset{\substack{\#\text{neutrons}\\\downarrow}}{10})(\overset{\substack{m_n\\\downarrow}}{1.674927498\times10^{-27}}) - 3.1547\times10^{-26}$$

$$\underset{\substack{\uparrow\\\text{mass defect}}}{\Delta m} = 2.559\times10^{-28}\,\text{Kg}$$

$$E = mc^2$$

$$E = (2.559\times10^{-28}\,\text{Kg})(3\times10^{8}\,\text{m/s})^2$$

$$E = 2.30\times10^{-11}\,\text{J}$$

$$19\text{ nucleons} \rightarrow \frac{2.30\times10^{-11}\,\text{J}}{19} = \boxed{1.2\times10^{-12}\,\text{J/nucleon}}$$

16) Which of the following would buffer systems would you most optimally choose to create a buffer of pH = 6.50? The Ka of $H_2B = 1x10^{-5}$ and the ka of $HB^- = 1x10^{-7}$.

A) B^{2-} / H_2B
[✓ B)] B^{2-} / HB^-
C) HB^- / H_2B
D) HB^- / HB_2
E) B^{2-} / HB_2

$$H_2B:\ pKa = -\log(1\times10^{-5}) = 5$$

buffer range : 4 – 6

$$HB^-:\ pKa = -\log(1\times10^{-7}) = 7$$

$$\text{buffer range}:\ 6-\underset{\substack{\uparrow\\6.5}}{}8$$

$$HB^-/B^{2-}$$

17) Calculate the molar solubility of Ag_2CO_3 at 25°C. Ksp = 8.1×10^{-12}

$$Ag_2CO_3 \rightleftharpoons 2Ag^+ + CO_3^{2-}$$

	$2Ag^+$	CO_3^{2-}
I	0	0
C	+2s	+s
E	2s	s

$$K_{sp} = [Ag^+]^2[CO_3^{2-}]$$

$$8.1\times10^{-12} = (2s)^2(s)$$

$$8.1\times10^{-12} = 4s^3$$

$$s = \sqrt[3]{\frac{8.1\times10^{-12}}{4}} = \boxed{1.27\times10^{-4} M}$$

18) Which of the following reactions would you expect to be spontaneous at high temperatures but nonspontaneous at low temperatures?

A) An exothermic reaction with $S^\circ_{reaction} < 0$
B) An endothermic reaction with $S^\circ_{reaction} < 0$
C) An exothermic reaction with $S^\circ_{reaction} > 0$
[✓ D)] An endothermic reaction with $S^\circ_{reaction} > 0$
E) Such a reaction does not exist

$\Delta G < 0$ when T↑

$\Delta G > 0$ when T↓

$$\Delta G = \overset{\oplus}{\Delta H} - \overset{\ominus}{T\Delta S}$$

endothermic

ΔS ↓ ⊕

19) Is MnO_4^- or Br_2 a stronger oxidizing agent? Explain.

$\boxed{MnO_4^-}$

* Strong oxidizing agents have <u>high</u> oxidation numbers

MnO_4^- → (+7)

Br_2 → (0)

* can also look at reduction potential table (higher on table = stronger oxidizing agent)

20) True or False: CaO is a more basic oxide than Rb_2O.

False oxide basicity ↑ down and to the left

(more metallic character = more basic oxide)

21) Consider the complex trans-$[Co(CH_3NH_2)_4Cl_2]NO_3$, what is the coordination number and the oxidation state, respectively, of the transition metal ion?

6 monodentate ligands → coordination number is $\boxed{6}$

$$\big[\underset{\substack{\downarrow \\ +3}}{Co}\,\underset{\substack{\downarrow \\ 0}}{(CH_3NH_2)_4}\,\underset{\substack{\downarrow \\ -2}}{Cl_2}\big]^{+} \quad NO_3^{-}$$

Co has an oxidation number of $\boxed{+3}$