1. In the reaction shown, 100.0 g $C_6H_{11}OH$ yielded 64.0 g C_6H_{10}. 1) what is the theoretical yield of the reaction, 2) what is the percent yield?, 3) what mass of $C_6H_{11}OH$ would produce 100.0g of C_6H_{10} if the percent yield is that determine in part 2?

$$C_6H_{10}OH \rightarrow C_6H_{10} + H_2O$$

(M) (a) $$\text{mass } C_6H_{10} = 100.0\,\text{g } C_6H_{11}OH \times \frac{1\,\text{mol } C_6H_{11}OH}{100.16\,\text{g } C_6H_{11}OH} \times \frac{1\,\text{mol } C_6H_{10}}{1\,\text{mol } C_6H_{11}OH}$$
$$\times \frac{82.146\text{g } C_6H_{10}}{1\,\text{mol } C_6H_{10}} = 82.01\,\text{g } C_6H_{10} = \text{theoretical yield}$$

(b) $$\text{percent yield} = \frac{64.0\,\text{g } C_6H_{10}\text{ produced}}{82.01\,\text{g } C_6H_{10}\text{ calculated}} \times 100\% = 78.0\%\text{ yield}$$

(c) $$\text{mass } C_6H_{11}OH = 100.0\,\text{g } C_6H_{10}\text{ produced} \times \frac{1.000\,\text{g calculated}}{0.780\,\text{g produced}} \times \frac{1\,\text{mol } C_6H_{10}}{82.15\,\text{g } C_6H_{10}}$$
$$\times \frac{1\,\text{mol } C_6H_{11}OH}{1\,\text{mol } C_6H_{10}} \times \frac{100.2\,\text{g } C_6H_{11}OH}{1\,\text{mol } C_6H_{11}OH} = 156\,\text{g } C_6H_{11}OH\text{ are needed}$$

2. A 99.8 mL sample of a solution that is 12.0% of KI by mass (d = 1.093 g/mL) is added to 96.7 mL of another solution that 14.0% $Pb(NO_3)_2$ by mass (d = 1.134 g/mL). How many grams of PbI_2 should form?

$$Pb(NO_3)_2 + 2KI\,(aq) \rightarrow PbI_2(s) + 2KNO_3\,(aq)$$

Here we must determine the amount of PbI_2 produced from each solute in this limiting reactant problem.

$$n_{PbI_2}\,(\text{from KI}) = 99.8\,\text{mL} \times \frac{1.093\,\text{g}}{1\,\text{mL soln}} \times \frac{0.120\,\text{g KI}}{1\,\text{g soln}} \times \frac{1\,\text{mol KI}}{166.00\,\text{g KI}} \times \frac{1\,\text{mol } PbI_2}{2\,\text{mol KI}} = 0.0394\,\text{mol}$$

$$n_{PbI_2}\,(\text{from } Pb(NO_3)_2) = 96.7\,\text{mL} \times \frac{1.134\,\text{g}}{1\,\text{mL soln}} \times \frac{0.140\,\text{g } Pb(NO_3)_2}{1\,\text{g soln}} \times \frac{1\,\text{mol } Pb(NO_3)_2}{331.2\,\text{g}} \times \frac{1\,\text{mol } PbI_2}{1\,\text{mol } Pb(NO_3)_2}$$
$$= 0.0464\,\text{mol } PbI_2$$

Then the mass of PbI_2 is computed from the smaller amount produced.

$$\text{mass } PbI_2 = 0.0394\,\text{mol } PbI_2 \times \frac{461.0\,\text{g } PbI_2}{1\,\text{mol } PbI_2} = 18.2\,\text{g } PbI_2$$

3. A 110.520 g sample of mineral water is analyzed for its magnesium content. The Mg^{2+} in the sample is first precipitated as $MgNH_4PO_4$ and this precipitate is converted to $Mg_2P_2O_7$ which is found to weight 0.0549 g. Express the quantity of magnesium in the sample in part per million (that is, in grams of Mg per million of grams of water).

Let us first determine the mass of Mg in the sample analyzed.

Conversion pathway approach:

$$\text{mass Mg} = 0.0549\text{ g Mg}_2\text{P}_2\text{O}_7 \times \frac{1\text{ mol Mg}_2\text{P}_2\text{O}_7}{222.55\text{ g Mg}_2\text{P}_2\text{O}_7} \times \frac{2\text{ mol Mg}}{1\text{ mol Mg}_2\text{P}_2\text{O}_7} \times \frac{24.305\text{ g}}{1\text{ mol Mg}} = 0.0120\text{ g Mg}$$

$$\text{ppm Mg} = 10^6\text{ g sample} \times \frac{0.0120\text{ g Mg}}{110.520\text{ g sample}} = 108\text{ ppm Mg}$$

Stepwise approach:

$$0.0549\text{ g Mg}_2\text{P}_2\text{O}_7 \times \frac{1\text{ mol Mg}_2\text{P}_2\text{O}_7}{222.55\text{ g Mg}_2\text{P}_2\text{O}_7} = 2.47\times10^{-4}\text{ mol Mg}_2\text{P}_2\text{O}_7$$

$$2.47\times10^{-4}\text{ mol Mg}_2\text{P}_2\text{O}_7 \times \frac{2\text{ mol Mg}}{1\text{ mol Mg}_2\text{P}_2\text{O}_7} = 4.93\times10^{-4}\text{ mol Mg}$$

$$4.93\times10^{-4}\text{ mol Mg} \times \frac{24.305\text{ g}}{1\text{ mol Mg}} = 0.0120\text{ g Mg}$$

$$\text{ppm Mg} = 10^6\text{ g sample} \times \frac{0.0120\text{ g Mg}}{110.520\text{ g sample}} = 108\text{ ppm Mg}$$

4. A 0.4324 g sample of a potassium hydroxide-lithium hydroxide mixture requires 28.28 mL of 0.3520 M HCl for its titration to the equivalence point. What is the mass percent lithium hydroxide in this mixture?

Let X_{KOH} = mass of KOH in grams and X_{LiOH} be the mass of LiOH in grams.

(Note: Molar masses: KOH = 56.1056 g mol^{-1} and LiOH = 23.9483 g mol^{-1})

moles of HCl = C×V = 0.3520 M × 0.02828 L = 0.009956 mol HCl

We can set up two equations for the two unknowns:

$X_{\text{KOH}} + X_{\text{LiOH}} = 0.4324$ g and since moles of HCl = moles of OH^- (Stoichiometry is 1:1)

$$0.009956\text{ mol OH}^- = \frac{X_{\text{KOH}}}{56.1056} + \frac{X_{\text{LiOH}}}{23.9483}$$

Make the substitution that $X_{\text{KOH}} = 0.4324\text{ g} - X_{\text{LiOH}}$

$$0.009956\text{ mol OH}^- = \frac{(0.4324 - X_{\text{LiOH}})}{56.1056} + \frac{X_{\text{LiOH}}}{23.9483} = \frac{0.4324}{56.1056} - \frac{X_{\text{LiOH}}}{56.1056} + \frac{X_{\text{LiOH}}}{23.9483}$$

Collect terms: $0.009956\text{ mol OH}^- = 0.007707\text{ mol OH}^- + 0.02393X_{\text{LiOH}}\text{ mol OH}^-$

$0.009956\text{ mol OH}^- - 0.007707\text{ mol OH}^- = 0.02393X_{\text{LiOH}}\text{ mol OH}^- = 0.002249\text{ mol OH}^-$

$X_{\text{LiOH}} = 0.09397$ g LiOH hence, $X_{\text{KOH}} = 0.4324\text{ g} - 0.09397\text{ g} = 0.3384\text{ g}$

$$\text{Mass \% LiOH} = \frac{0.09397\,g}{0.4324\,g}\times100\% = 21.73\% \quad \text{Mass \% KOH} = \frac{0.3384\,g}{0.4324\,g}\times100\% = 78.26\%$$

5. At high temperatures, solid NaClO3 produces NaCl and O_2 gas. A 0.8756 g sample of impure $NaClO_3$ was heated till the production of oxygen ceased. The oxygen was collected over water and occupied a volume of 57.2 mL at 23.0 C and 734 mmHg. Calculate the mass percentage of $NaClO_3$ in the original sample. The vapor pressure of water ies 21.07 mmHg at 23 C.

$$2NaClO_3 \xrightarrow{\Delta} 2NaCl + 3O_2$$

The pressure of O_2 is determined by subtracting the known vapor pressure of water at the given temperature from the measured total pressure.

$P_{O2} = P_{TOT} - P_{H2O} = 734\text{ torr} - 21.07\text{ torr} = 713\text{ torr}$
$P_{atm} = 713\text{ mmHg} / 760\text{ mmHg} = 0.938\text{ atm}$

$$\text{mol } O_2 = \frac{PV}{RT} = \frac{(0.938\text{ atm})(0.0572\text{ L})}{(0.08206\text{ L}\cdot\text{atm}\cdot\text{K}^{-1})(296\text{ K})} = 0.00221\text{ mol}$$

Mass of $NaClO_3$ is then determined as follows:

$$0.00221\text{ mol } O_2 \times \frac{2\text{ mol NaClO}_3}{3\text{ mol } O_2} \times \frac{106.44\text{ g}}{1\text{ mol NaClO}_3} = 0.1568\text{ g NaClO}_3$$

$$\%NaClO_3 = \frac{0.1568\text{ g}}{0.8765\text{ g}} \times 100 = 17.9\%$$

6. Gas cylinder A has a volume of 48.2 L and contains N_2 at 8.35 atm at 25C. Gas cylinder B, of unknown volume, contains He at 9.50 atm and 25C. When the two cylinders are connected and the gases mixed, the pressure in each cylinder becomes 8.71. What is the volume of the cylinder B?

The amount of $N_2(g)$ plus the amount of He(g) equals the total amount of gas. We use this equality, and substitute with the ideal gas law, letting V symbolize the volume of cylinder B.

$$n_{N_2} + n_{He} = n_{total} \quad \text{becomes} \quad P_{N_2} \times V_{N_2} + P_{He} \times V_{He} = P_{total} \times V_{total}$$

since all temperatures are equal.

Substitution gives (8.35 atm × 48.2 L) + (9.50 atm × V) = 8.71 atm (48.2 L + V)

$$402\text{ L atm} + 9.50\,V = 420\text{ L atm} + 8.71\,V \qquad V = \frac{420 - 402}{9.50 - 8.71} = 23\text{ L}$$

7. A bomb calorimetry experiment is performed with xylose $C_5H_{10}O_5$ as combustible substance. The data obtained were:

Mass of xylose burned	1.183 g
Heat capacity of calorimeter	4.728 kJ/C
Initial T	23.39C
Final calorimeter T	27.19C

(a) what is the heat of combustion of xylose in kJ/mol?
(b) (b) write the chemical equation for the complete combustion of xylose and represent the value of ΔH in this equation (Assume that ΔU~ΔH).

(a)

$$\frac{\text{heat}}{\text{mass}} = \frac{\text{heat cap.} \times \Delta t}{\text{mass}} = \frac{4.728 \text{ kJ}/^\circ\text{C} \times (27.19 - 23.29)^\circ\text{C}}{1.183 \text{ g}} = 15.6 \text{ kJ}/\text{g xylose}$$

$$\Delta H = \text{heat given off}/\text{g} \times M(\text{g}/\text{mol}) = \frac{-15.6 \text{ kJ}}{1 \text{ g } C_5H_{10}O_5} \times \frac{150.13 \text{ g } C_5H_{10}O_5}{1 \text{ mol}}$$

$$\Delta H = -2.34 \times 10^3 \text{ kJ/mol } C_5H_{10}O_5$$

(b) $C_5H_{10}O_5(g) + 5O_2(g) \rightarrow 5CO_2(g) + 5H_2O(l)$ $\quad \Delta H = -2.34 \times 10^3$ kJ

8. Use the Hess law to determine ΔH^0 for the reaction

$CO(g) + \frac{1}{2} O_{2(g)} \rightarrow CO_2$, given that

$C(s) + \frac{1}{2} O_2(g) \rightarrow CO(g)$ $\quad \Delta H^0 = -110.54$kJ
$C(s) + O_2(g) \rightarrow CO_2(g)$ $\quad \Delta H^0 = -393.51$kJ

$$\begin{array}{lll} -(1) & CO(g) \rightarrow C(\text{graphite}) + \tfrac{1}{2}O_2(g) & \Delta H^\circ = +110.54 \text{ kJ} \\ +(2) & C(\text{graphite}) + O_2(g) \rightarrow CO_2(g) & \Delta H^\circ = -393.51 \text{ kJ} \\ \hline & CO(g) + \tfrac{1}{2}O_2(g) \rightarrow CO_2(g) & \Delta H^\circ = -282.97 \text{ kJ} \end{array}$$

9. Use the Hess law and the following data

$$\begin{array}{ll} CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) & \Delta H^0 = -802kJ \\ CH_4(g) + CO_2(g) \rightarrow 2CO(g) + 2H_2(g) & \Delta H^0 = +247kJ \\ CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g) & \Delta H^0 = +206kJ \end{array}$$

To determine ΔH^0 for the following reaction:

$$CH_4(g) + 1/2O_2(g) \rightarrow CO(g) + 2H_2(g)$$

$$\begin{array}{ll} CH_4(g)+CO_2(g)\rightarrow 2CO(g)+2H_2(g) & \Delta H^\circ = +247 \text{ kJ} \\ 2CH_4(g)+2H_2O(g)\rightarrow 2CO(g)+6H_2(g) & \Delta H^\circ = 2(+206 \text{ kJ}) = +412 \text{ kJ} \\ CH_4(g)+2O_2(g)\rightarrow CO_2(g)+2H_2O(g) & \Delta H^\circ = -802 \text{ kJ} \\ \hline 4CH_4(g)+2O_2(g)\rightarrow 4CO(g)+8H_2(g) & \Delta H^\circ = -143 \text{ kJ} \\ \div 4 \text{ produces } CH_4(g)+\tfrac{1}{2}O_2(g)\rightarrow CO(g)+2H_2(g) & \Delta H^\circ = -35.8 \text{ kJ} \end{array}$$

10. Without calculation, arrange the following electromagnetic radiation sources in order of increasing frequency.

a) Red traffic light
b) a 91.9 MHz radio transmitter
c) light with a frequency of 3.0×10^{-14} s^{-1}
d) light with a wavelength of 49 nm.

Increasing frequency is decreasing wavelength. Radio waves have the longest wavelengths/ lowest frequencies (b), followed by infrared light (c), follwed by visible light (a), and finally UV radiation (d). Thus, the frequency increases from left to right in the following order: (b) < (c) < (a) < (d).

11. Use the Planck's equation to determine:

a) the energy in joules per photon of a radiation of frequency 7.39 x 10^{15} sec^{-1}
b) the energy in kJ/mol of a radiation of frequency 1.97 x 10^{14} sec^{-1}

(a) $E = h\nu = 6.626\times10^{-34}\ \text{J s}\times7.39\times10^{15}\ \text{s}^{-1} = 4.90\times10^{-18}\ \text{J/photon}$

(b) $E_m = 6.626\times10^{-34}\ \text{J s}\times1.97\times10^{14}\ \text{s}^{-1}\times\frac{6.022\times10^{23}\ \text{photons}}{\text{mol}}\times\frac{1\ \text{kJ}}{1000\ \text{J}} = 78.6\ \text{kJ/mol}$

12. What is the ground state electron configuration for each of the following elements

Te,
Cs,
Se,
Pt,
Os,
Cr

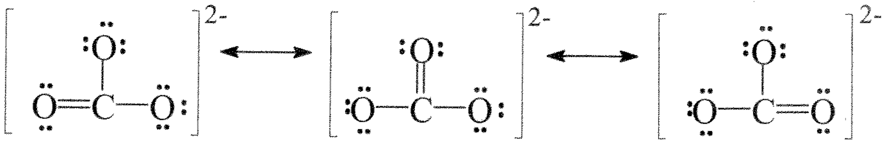
(a) Te: $[\text{Kr}]4d^{10}5s^{2}5p^{4}$
(b) Cs: $[\text{Xe}]6s^{1}$
(c) Se: $[\text{Ar}]4s^{2}3d^{10}4p^{4}$
(d) *Pt: $[\text{Xe}]6s^{2}\,4f^{14}\,5d^{8}$
(e) Os: $[\text{Xe}]6s^{2}4f^{14}5d^{6}$
(f) Cr: $[\text{Ar}]4s^{1}3d^{5}$

$4s^{2}3d^{5}$ also OK

13. Which of the following species requires a resonance hybrid for its Lewis structure?: explain

CO_2, OCl^-, CO_3^{2-}, OH^-

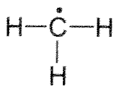
In CO_3^{2-}, there are $4+(3\times6)+2=24$ valence electrons, or 12 electron pairs (see below).



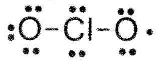
14. Write plausible Lewis structure for the following odd-electron species:

CH_3, ClO_2, NO_3.

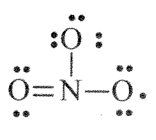
(a) CH_3 has a total of $(3\times1)+4=7$ valence electrons, or 3 electron pairs and a lone electron. C is the central atom. A plausible Lewis structure is shown on the right.



(b) ClO_2 has a total of $(2\times6)+7=19$ valence electrons, or 9 electron pairs and a lone electron. Cl is the central atom. A plausible Lewis structure is:


$:\ddot{\underset{..}{O}}-\ddot{\underset{..}{Cl}}-\ddot{\underset{..}{O}}\cdot$

(c) NO_3 has a total of $(3\times6)+5=23$ valence electrons, or 11 electron pairs, plus a lone electron. N is the central atom. A plausible Lewis structure is shown to the right. Other resonance forms can also be

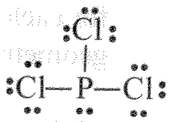


15. Use VSEPR to predict the geometric shapes of the following molecules and ions:

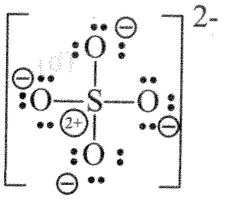
PCl_3, SO_4^{2-}, $SOCl_2$, SO_3, BrF_4^+

The AX_nE_m designations that are cited below are to be found in Table 11.1 of the text, along with a sketch and a picture of a model of each type of structure.

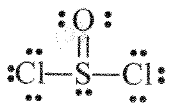
(a) PCl_3 is a trigonal pyramid. The molecule is of the AX_3E type, and has a tetrahedral electron-group geometry and a trigonal pyramid shape.



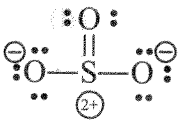
(b) SO_4^{2-} has a tetrahedral shape. The ion is of the type AX_4, and has a tetrahedral electron-group geometry and a tetrahedral shape. The other resonance forms of the sulfate ion have the same shape.



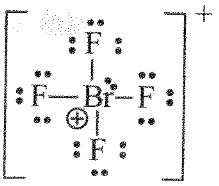
(c) $SOCl_2$ has a trigonal pyramidal shape. This molecule is of the AX_3E type and has a tetrahedral electron-group geometry and a trigonal pyramidal shape.



(d) SO_3 has a trigonal planar shape. The molecule is of the AX_3 type, with a trigonal planar electron-group geometry and molecular shape. The other resonance contributors have the same shape.



(e) BrF_4^+ has a distorted see-saw shape. The molecule is of the AX_4E type, with a trigonal bipyramid electron-group geometry and a see-saw molecular shape.



16.

17. Consider the molecules NO^+ and N_2^+, and use molecular orbitals:

a) write the MO configuration of each ion (ignore the 1s electron);
b) predict the bond order of each ion;
c) which of these ions is paramagnetic?
d) Which of these ions has the greater bond length?

18) A 0.682 g sample of ICl(g) is placed in a 625 mL vessel at 682K. When equilibrium is reached between the ICl(g) and $I_2(g)$ and $Cl_2(g)$ formed by its dissociation, 0.0383g I_2 is present. What is the Kc for this reaction?

$$[\mathrm{ICl}]_{\mathrm{initial}} = \frac{0.682\ \mathrm{g\ ICl} \times \frac{1\ \mathrm{mol\ ICl}}{162.36\ \mathrm{g\ ICl}}}{0.625\ \mathrm{L}} = 6.72\times10^{-3}\ \mathrm{M}$$

Reaction:	$2\,ICl(g)$	$\rightleftharpoons$ $I_2(g)$	+	$Cl_2(g)$
Initial:	6.72×10^{-3} M	0 M		0 M
Change	$-2x$	$+x$		$+x$
Equilibrium	6.72×10^{-3} M $-2x$	x		x

$$[\mathrm{I_2}]_{\mathrm{equil}} = \frac{0.0383\ \mathrm{g\ I_2} \times \frac{1\ \mathrm{mol\ I_2}}{253.808\ \mathrm{g\ I_2}}}{0.625\,\mathrm{L}} = 2.41\times10^{-4}\ \mathrm{M} \quad = x$$

$$K_c = \frac{x \cdot x}{(6.72\times10^{-3} - 2x)^2} = \frac{(2.41\times10^{-4})^2}{(6.72\times10^{-3} - 2(2.41\times10^{-4}))^2} = \mathrm{XXXXXX}^{-6} \quad 1.49\ \mathrm{x}\ 10(-3)$$

19) Is a mixture of 0.0205 mol of $NO_2(g)$ and 0.750 mol N_2O_4 in a 5.25 L flask at 25C at the equilibrium? If not in which direction the reaction will proceed?

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \quad Kc = 4.61 \times 10^{-3} \text{ at } 25C$$

We compute the value of Q_c for the given amounts of product and reactants.

$$Q_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{\left(\frac{0.0205\,\text{mol}\,NO_2}{5.25\,\text{L}}\right)^2}{\frac{0.750\,\text{mol}\,N_2O_4}{5.25\,\text{L}}} = 1.07 \times 10^{-4} < K_c = 4.61 \times 10^{-3}$$

The mixture described cannot be maintained indefinitely. In fact, because $Q_c < K_c$, the reaction will proceed to the right, that is, toward products, until equilibrium is established. If E_a is large, however, it may take some time to reach equilibrium.

20) Cadmium metal is added to 0.350 L of an aqueous solution in which $[Cr^{3+}] = 1.00M$. What are the concentrations of the different ionic species at equilibrium? What is the minimum mass of cadmium metal required to establish this equilibrium?

$$Cr^{3+}(aq) + Cd(s) \rightleftharpoons Cr^{2+}(aq) + Cd^{2+}(aq) \text{ (unbalanced)} \quad Kc = 0.288$$

We organize the solution around the balanced chemical equation.

Equation:	$2\,Cr^{3+}(aq)$ + $Cd(s)$	$\rightleftharpoons$	$2\,Cr^{2+}(aq)$	+ $Cd^{2+}(aq)$
Initial:	1.00 M		0 M	0 M
Changes:	$-2x$ M		$+2x$	$+x$
Equil:	$(1.00-2x)$ M		$2x$	x

$$K_c = \frac{[Cr^{2+}]^2[Cd^{2+}]}{[Cr^{3+}]^2} = \frac{(2x)^2(x)}{(1.00-2x)^2} = 0.288$$

Via successive approximations, one obtains $x = 0.257\,\text{M}$

Therefore, at equilibrium, $[Cd^{2+}] = 0.257$ M, $[Cr^{2+}] = 0.514$ M and $[Cr^{3+}] = 0.486$ M

Minimum mass of Cd(s) = 0.350L × 0.257 M × 112.41 g/mol = 10.1 g of Cd metal

21. The acid CH_3CH_2COOH is 0.42% ionized in 0.80M solution. Calculate the value of Ka

The answer is (a). If $HC_3H_5O_2$ is 0.42% ionized for a 0.80 M solution, then the concentration of the acid at equilibrium is $(0.80 \times 0.0042) = 0.00336$. The equilibrium expression for the dissociation of $HC_3H_5O_2$ is:

$$K_a = \frac{[H_3O^+][C_3H_5O_2^-]}{[HC_3H_5O_2]} = \frac{(0.00336)(0.00336)}{(0.800 - 0.00336)} = 1.42 \times 10^{-5}$$

22. How many mL of concentrated HCl(aq) (36% HCl by mass d = 1.18g/mL) are required to produce 12.5 mL of a solution with pH = 2.10?

First determine the amount of HCl, and then the volume of the concentrated solution required.

$$\text{amount HCl} = 12.5\ \text{L} \times \frac{10^{-2.10}\ \text{mol H}_3\text{O}^+}{1\ \text{L soln}} \times \frac{1\ \text{mol HCl}}{1\ \text{mol H}_3\text{O}^+} = \cancel{0.099\ \text{mol HCl}}$$ 9.9 x 10(-5)

mL!!

$$V_{\text{solution}} = \cancel{0.099}\ \text{mol HCl} \times \frac{36.46\ \text{g HCl}}{1\ \text{mol HCl}} \times \frac{100.0\ \text{g soln}}{36.0\ \text{g HCl}} \times \frac{1\ \text{mL soln}}{1.18\ \text{g soln}} = \cancel{8.5\ \text{mL soln}}$$ 8.5 x 10(-3)

9.9 x 10(-5)

23. A particular household ammonia solution (d = 0.97 g/mL) is 6.8% $NH_3$by mass. How many milliliters of this solution should be diluted with water to produce 625 mL of a solution with pH = 11.55?

(M) First we determine $\left[OH^-\right]$ which, because of the stoichiometry of the reaction, equals$\left[NH_4^+\right]$.

$$pOH = 14.00 - pH = 14.00 - 11.55 = 2.45 \qquad \left[OH^-\right] = 10^{-pOH} = 10^{-2.45} = 3.5\times10^{-3}\,M = \left[NH_4^+\right]$$

We solve for S, the concentration of NH_3 in the 0.625 L solution prior to dissociation.

Equation:	$NH_3(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$NH_4^+(aq)$	+	$OH^-(aq)$
Initial:	S M		—		0 M		≈0 M
Changes:	−0.0035 M		—		+0.0035 M		+0.0035 M
Equil:	$(S-0.0035)$ M		—		0.0035 M		0.0035 M

$$K_b = \frac{\left[NH_4^+\right]\left[OH^-\right]}{\left[NH_3\right]} = 1.8\times10^{-5} = \frac{(0.0035)^2}{(S-0.0035)}$$

$$(0.0035)^2 = 1.8\times10^{-5}(S-0.0035) = 1.225\times10^{-5} = 1.8\times10^{-5}S - 6.3\times10^{-8}$$

$$S = \frac{1.225\times10^{-5} + 6.3\times10^{-8}}{1.8\times10^{-5}} = 0.68\ M$$

Now we determine the volume of household ammonia needed

$$V_{\text{ammonia}} = 0.625\ \text{L soln}\times\frac{0.68\ \text{mol NH}_3}{1\ \text{L soln}}\times\frac{17.03\ \text{g NH}_3}{1\ \text{mol NH}_3}\times\frac{100.0\ \text{g soln}}{6.8\ \text{g NH}_3}\times\frac{1\ \text{mL soln}}{0.97\ \text{g soln}}$$

$$= 1.1\times10^2\ \text{mL household ammonia solution}$$

24. What concentration of NH_3should be present in a solution with $[NH_4^+] = 0.732M$ to produce a buffer solution with pH = 9.12? For NH_3 $K_b = 1.8 \times 10^{-5}$.

(E) We use the Henderson-Hasselbalch equation to find the required $[NH_3]$.

$$pK_b = -\log(1.8\times10^{-5}) = 4.74$$

$$pK_a = 14.00 - pK_b = 14.00 - 4.74 = 9.26 \qquad pH = 9.12 = 9.26 + \log\frac{[NH_3]}{\left[NH_4^+\right]}$$

$$\frac{[NH_3]}{\left[NH_4^+\right]} = 10^{-0.14} = 0.72 \qquad [NH_3] = 0.72\times\left[NH_4^+\right] = 0.72\times0.732\,M = 0.53\,M$$

25. Calculate the pH at the points of titration of 25.00 mL of 0.160M HCl when (a) 10.00 mL and (b) 15.00 mL of 0.242M KOH have been added.

First we calculate the amount of HCl. The relevant titration reaction is

$$\mathrm{HCl(aq)} + \mathrm{KOH(aq)} \rightarrow \mathrm{KCl(aq)} + \mathrm{H_2O(l)}$$

$$\text{amount HCl} = 25.00\ \text{mL} \times \frac{0.160\ \text{mmol HCl}}{1\ \text{mL soln}} = 4.00\ \text{mmol HCl} = 4.00\ \text{mmol H}_3\text{O}^+ \text{present}$$

Then, in each case, we calculate the amount of OH^- that has been added, determine which ion, $OH^-(aq)$ or $H_3O^+(aq)$, is in excess, compute the concentration of that ion, and determine the pH.

(a) $$\text{amount OH}^- = 10.00\ \text{mL} \times \frac{0.242\ \text{mmol OH}^-}{1\ \text{mL soln}} = 2.42\ \text{mmol OH}^-;\ \ \text{H}_3\text{O}^+ \text{ is in excess.}$$

$$[\text{H}_3\text{O}^+] = \frac{4.00\ \text{mmol H}_3\text{O}^+ - \left(2.42\ \text{mmol OH}^- \times \dfrac{1\ \text{mmol H}_3\text{O}^+}{1\ \text{mmol OH}^-}\right)}{25.00\ \text{mL originally} + 10.00\ \text{mL titrant}} = 0.0451\ \text{M}$$

$$\text{pH} = -\log(0.0451) = 1.346$$

$$\text{amount OH}^- = 15.00\ \text{mL} \times \frac{0.242\ \text{mmol OH}^-}{1\ \text{mL soln}} = 3.63\ \text{mmol OH}^-;\ \ \text{H}_3\text{O}^+ \text{ is in excess.}$$

$$[\text{H}_3\text{O}^+] = \frac{4.00\ \text{mmol H}_3\text{O}^+ - \left(3.63\ \text{mmol OH}^- \times \dfrac{1\ \text{mmol H}_3\text{O}^+}{1\ \text{mmol OH}^-}\right)}{25.00\ \text{mL originally} + 15.00\ \text{mL titrant}} = 0.00925\ \text{M}$$

$$\text{pH} = -\log(0.00925) = 2.034$$

26. Excess $Ca(OH)_2$ is shaken with water to produce a saturated solution. A 50.00 mL sample of the clear saturated solution is withdrawn and requires 10.7 mL of 0.1032 M HCl for its titration. What is Ksp for $Ca(OH)_2$?

The titration reaction is $\mathrm{Ca(OH)_2(aq)} + \mathrm{2HCl(aq)} \longrightarrow \mathrm{CaCl_2(aq)} + \mathrm{2H_2O(l)}$

$$\left[\text{OH}^-\right] = \frac{10.7\ \text{mL HCl} \times \dfrac{1\ \text{L}}{1000\ \text{mL}} \times \dfrac{0.1032\ \text{mol HCl}}{1\ \text{L}} \times \dfrac{1\ \text{mol OH}^-}{1\ \text{mol HCl}}}{50.00\ \text{mL Ca(OH)}_2\ \text{soln} \times \dfrac{1\ \text{L}}{1000\ \text{mL}}} = 0.0221\ \text{M}$$

In a saturated solution of $\mathrm{Ca(OH)_2}$, $\left[\text{Ca}^{2+}\right] = \left[\text{OH}^-\right] \div 2$

$K_{sp} = \left[\text{Ca}^{2+}\right]\left[\text{OH}^-\right]^2 = (0.0221 \div 2)(0.0221)^2 = 5.40 \times 10^{-6}$ (5.5×10^{-6} in Appendix D).

27. A 25.00 mL sample of clear saturated solution of PbI_2 requires 13.3 mL of a certain $AgNO_3$(aq) for its titration (precipitation of AgI). What is the molarity of this $AgNO_3$ (aq)? Ksp (PbI_2) = 7.1×10^{-9}

First we determine $\left[I^-\right]$ in the saturated solution.

$$K_{sp} = \left[Pb^{2+}\right]\left[I^-\right]^2 = 7.1 \times 10^{-9} = (s)(2s)^2 = 4s^3 \qquad s = 1.2 \times 10^{-3}\,M$$

The $AgNO_3$ reacts with the I^- in this saturated solution in the titration.

$Ag^+(aq) + I^-(aq) \rightarrow AgI(s)$ We determine the amount of Ag^+ needed for this titration, and then $\left[AgNO_3\right]$ in the titrant.

$$\text{moles } Ag^+ = 0.02500\,L \times \frac{1.2 \times 10^{-3}\,\text{mol } PbI_2}{1\,L\text{ soln}} \times \frac{2\text{ mol } I^-}{1\,\text{mol } PbI_2} \times \frac{1\,\text{mol } Ag^+}{1\,\text{mol } I^-} = 6.0 \times 10^{-5}\,\text{mol } Ag^+$$

$$AgNO_3\text{ molarity} = \frac{6.0 \times 10^{-5}\,\text{mol } Ag^+}{0.0133\,L\text{ soln}} \times \frac{1\,\text{mol } AgNO_3}{1\,\text{mol } Ag^+} = 4.5 \times 10^{-3}\,M$$

28. At 298K, for the reaction

$$2H^+\,(aq) + 2Br^-\,(aq) + 2NO_2(g) \rightarrow Br_2(l) + 2HNO_2(aq)$$

ΔH^0 = -61.6 kJ/mol and the standard molar entropies are H^+(aq) = 0 J/K; Br^-(aq) = 82.4 J/K; NO_2(g) = 240.1 J/K; Br_2(l) = 152.2 J/K; HNO_2(aq) = 135/6 J/K. Determine ΔG^0 at 298K and whether the reaction proceeds spontaneously in the forward or reverse direction when reactants and products are in their standard states.

(a) $\Delta S^\circ = S^\circ\left[Br_2(l)\right] + 2S^\circ\left[HNO_2(aq)\right] - 2S^\circ\left[H^+(aq)\right] - 2S^\circ\left[Br^-(aq)\right] - 2S^\circ\left[NO_2(g)\right]$

$= 152.2\text{ J/K} + 2(135.6\text{ J/K}) - 2(0\text{ J/K}) - 2(82.4\text{ J/K}) - 2(240.1\text{ J/K}) = -221.6\text{ J/K}$

$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ = -61.6 \times 10^3\,J - (298\,K)(-221.6\text{ J/K}) = +4.4 \times 10^3\,J = +4.4\,kJ$

(b) The reaction does not proceed spontaneously in the forward direction when reactants and products are in their standard states, because the value of ΔG° is greater than zero.

29. In the synthesis of gaseous CH_3OH from CO(g) and $H_2(g)$ the following equilibrium concentrations were determined at 483K: [CO] = 0.0911M, $[H_2]$ = 0.0822M, and $[CH_3OH]$ = 0.00892M.Calculate the equilibrium constant and Gibbs energy for this reaction.

In this problem we are asked to determine the equilibrium constant and the change in Gibbs free energy for the reaction between carbon monoxide and hydrogen to yield methanol. The equilibrium concentrations of each reagent at 483K were provided. We proceed by first determining the equilibrium constant. Gibbs free energy can be calculated using $\Delta G^o = -RT \ln K$.

Stepwise approach:

First determine the equilibrium constant for the reaction at 483K:

$$\mathrm{CO(g){+}2H_2(g) \rightleftharpoons CH_3OH(g)}$$

$$K = \frac{[CH_3OH(g)]}{[CO(g)][H_2(g)]} = \frac{0.00892}{0.0911 \times 0.0822^2} = 14.5$$

Now use $\Delta G^o = -RT \ln K$ to calculate the change in Gibbs free energy at 483 K:

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

$$\Delta G^o = -8.314 \times 483 \times \ln(14.5)\mathrm{Jmol^{-1}} = -1.1 \times 10^4\,\mathrm{Jmol^{-1}}$$

$$\Delta G^o = -11\mathrm{kJmol^{-1}}$$

Conversion pathway approach:

$$K = \frac{[CH_3OH(g)]}{[CO(g)][H_2(g)]} = \frac{0.00892}{0.0911 \times 0.0822^2} = 14.5$$

$$\Delta G^o = -RT \ln K = -8.314 \times 483 \times \ln(14.5)\mathrm{Jmol^{-1}} = -1.1 \times 10^4\,\mathrm{Jmol^{-1}}$$

$$\Delta G^o = -11\mathrm{kJmol^{-1}}$$

30. Assume that all reactants and products are in their standard states and use data from the table in the data sheet to predict whether a spontaneous reaction will occur in the forward direction in each case.

$\mathrm{Sn(s)} + \mathrm{Pb^{2+}(aq)} \rightarrow \mathrm{Sn^{2+(}aq)} + \mathrm{Pb(s)}$
$\mathrm{Cu^{=2}(aq)} + \mathrm{2I^{-}(aq)} \rightarrow \mathrm{Cu(s)} + \mathrm{I_2(s)}$
$\mathrm{4NO_3^{-}(aq)} + \mathrm{4H^{+}(aq)} \rightarrow \mathrm{3O_2(g)} + \mathrm{4NO(g)} + \mathrm{2H_2O(l)}$
$\mathrm{O_3(g)} + \mathrm{Cl^{-}(aq)} \rightarrow \mathrm{OCl^{-}(aq)} + \mathrm{O_2(g)}$ (basic solution)

(a) Oxidation: $\mathrm{Sn(s)} \rightarrow \mathrm{Sn^{2+}(aq)} + 2e^-$ $\quad -E° = +0.137$ V
Reduction: $\mathrm{Pb^{2+}(aq)} + 2e^- \rightarrow \mathrm{Pb(s)}$ $\quad E° = -0.125$ V
Net: $\mathrm{Sn(s)} + \mathrm{Pb^{2+}(aq)} \rightarrow \mathrm{Sn^{2+}(aq)} + \mathrm{Pb(s)}$ $\quad E°_{\mathrm{cell}} = +0.012$ V $\quad$ Spontaneous

(b) Oxidation: $\mathrm{2I^-(aq)} \rightarrow \mathrm{I_2(s)} + 2e^-$ $\quad -E° = -0.535$ V
Reduction: $\mathrm{Cu^{2+}(aq)} + 2e^- \rightarrow \mathrm{Cu(s)}$ $\quad E° = +0.340$ V
Net: $\mathrm{2I^-(aq)} + \mathrm{Cu^{2+}(aq)} \rightarrow \mathrm{Cu(s)} + \mathrm{I_2(s)}$ $\quad E°_{\mathrm{cell}} = -0.195$ V $\quad$ Nonspontaneous

(c) Oxidation: $\{\mathrm{2H_2O(l)} \rightarrow \mathrm{O_2(g)} + \mathrm{4H^+(aq)} + 4e^-\} \times 3$ $\quad -E° = -1.229$ V
Reduction: $\{\mathrm{NO_3^-(aq)} + \mathrm{4H^+(aq)} + 3e^- \rightarrow \mathrm{NO(g)} + \mathrm{2H_2O(l)}\} \times 4$ $\quad E° = +0.956$ V
Net: $\mathrm{4NO_3^-(aq)} + \mathrm{4H^+(aq)} \rightarrow \mathrm{3O_2(g)} + \mathrm{4NO(g)} + \mathrm{2H_2O(l)}$ $\quad E°_{\mathrm{cell}} = -0.273$ V
Nonspontaneous

(d) Oxidation: $\mathrm{Cl^-(aq)} + \mathrm{2OH^-(aq)} \rightarrow \mathrm{OCl^-(aq)} + \mathrm{H_2O(l)} + 2e^-$ $\quad -E° = -0.890$ V
Reduction: $\mathrm{O_3(g)} + \mathrm{H_2O(l)} + 2e^- \rightarrow \mathrm{O_2(g)} + \mathrm{2OH^-(aq)}$ $\quad E° = +1.246$ V
Net: $\mathrm{Cl^-(aq)} + \mathrm{O_3(g)} \rightarrow \mathrm{OCl^-(aq)} + \mathrm{O_2(g)}$ (basic solution) $\quad E°_{\mathrm{cell}} = +0.356$ V
Spontaneous

31. A voltaic cell represented by the following cell diagram has E_{cell} = 1.250V. What must be $[Ag^{+}]$ in the cell?

$$Zn(s)/Zn^{2+}(1.00M)//Ag^{+}(xM)/Ag(s)$$

In this problem we are asked to determine the concentration of $[Ag^{+}]$ ions in trochemical cell that is not under standard conditions. We proceed by first determining E^{o}_{cell}. Using the Nerst equation and the known value of E, we can then calculate the concentration of $[Ag^{+}]$.

Stepwise approach:

First, determine E^{o}_{cell}:

$$\text{Oxidation: } Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-} \qquad -E^{\circ} = +0.763\,V$$

$$\text{Reduction: } \{Ag^{+}(aq) + e^{-} \rightarrow Ag(s)\} \times 2 \qquad E^{\circ} = +0.800\,V$$

$$\text{Net: } Zn(s) + 2Ag^{+}(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s) \qquad E^{\circ}_{cell} = +1.563\,V$$

Use the Nerst equation and the known value of E to solve for $[Ag]^{+}$:

$$E = E^{\circ}_{cell} - \frac{0.0592}{n}\log\frac{[Zn^{2+}]}{[Ag^{+}]^{2}} = +1.563\,V - \frac{0.0592}{2}\log\frac{1.00}{x^{2}} = +1.250\,V$$

$$\log\frac{1.00\,M}{x^{2}} = \frac{-2\times(1.250-1.563)}{0.0592} = 10.6;\quad x = \sqrt{2.\underline{5}\times10^{-11}} = 5\times10^{-6}\ M$$

Therefore, $[Ag^{+}] = 5 \times 10^{-6}$ M

Conversion pathway approach:

$$\text{Oxidation: } Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-} \qquad -E^{\circ} = +0.763\,V$$

$$\text{Reduction: } \{Ag^{+}(aq) + e^{-} \rightarrow Ag(s)\} \times 2 \qquad E^{\circ} = +0.800\,V$$

$$\text{Net: } Zn(s) + 2Ag^{+}(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s) \qquad E^{\circ}_{cell} = +1.563\,V$$

$$E = E^{\circ}_{cell} - \frac{0.0592}{n}\log\frac{[Zn^{2+}]}{[Ag^{+}]^{2}} \Rightarrow \log\frac{[Zn^{2+}]}{[Ag^{+}]^{2}} = -\frac{n}{0.0592}(E - E^{o}_{cell})$$

$$[Ag^{+}]^{2} = \frac{[Zn^{2+}]}{10^{-\frac{n}{0.0592}(E-E^{o}_{cell})}} \Rightarrow [Ag^{+}] = \sqrt{\frac{[Zn^{2+}]}{10^{-\frac{n}{0.0592}(E-E^{o}_{cell})}}}$$

$$[Ag^{+}] = \sqrt{\frac{1.00}{10^{-\frac{2}{0.0592}(1.250-1.563)}}} = 5\times10^{-6}$$