

- (10) 1. The sodium D-line is actually a pair of closely spaced spectroscopic lines seen in the emission spectrum of sodium atoms. The wavelengths are centred at 589.3 nm. The intensity of this emission makes it the major source of light and causes the yellow colour in the sodium arc light. If a sodium arc light is to produce 1.000 kilowatt (1000 J/s) of radiant energy at this wavelength, what amount (mol and g) of sodium atoms must emit photons per second?

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^8 \frac{\text{m}}{\text{s}})}{(589.3 \times 10^{-9} \text{ m})}$$

$$= 3.37 \times 10^{-19} \text{ J}$$

[5]

$$E_T = \frac{E}{\text{photon}} \cdot \# \text{ photons}$$

$$1000 \text{ J} = 3.37 \times 10^{-19} \frac{\text{J}}{\text{photon}} \cdot \# \text{ photons}$$

$$\# \text{ photons} = 2.96 \times 10^{21}$$

each photon comes from 1 Na atom

$$\therefore n_{\text{Na}} = \frac{2.96 \times 10^{21}}{6.022 \times 10^{23}} = \boxed{4.92 \times 10^{-3} \text{ mol}}$$

$$m_{\text{Na}} = n \cdot MM = (4.92 \times 10^{-3} \text{ mol}) \left(22.99 \frac{\text{g}}{\text{mol}} \right) = \boxed{0.113 \text{ g}}$$

- (b) When ultraviolet light of wavelength 131 nm strikes a polished nickel surface, the velocity of the ejected electrons is measured to be 1.24×10^6 m/s. Calculate the binding energy (ϕ) for nickel.

[5]

$$KE = h\nu - \phi$$

$$\phi = h\nu - KE$$

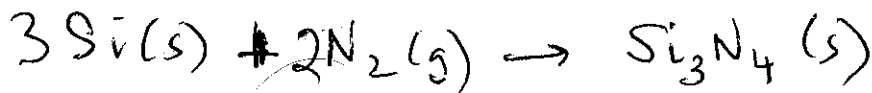
$$= \frac{hc}{\lambda} - \frac{1}{2}mv^2$$

$$= \frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^8 \frac{\text{m}}{\text{s}})}{131 \times 10^{-9} \text{ m}} - \frac{1}{2}(9.11 \times 10^{-31} \text{ kg})(1.24 \times 10^6 \frac{\text{m}}{\text{s}})^2$$

$$= 1.52 \times 10^{-18} \text{ J}$$

$$\text{or } 914 \frac{\text{kJ}}{\text{mol}}$$

- (10) 2. (a) Silicon nitride, a valuable ceramic, is made by the direct combination of silicon and nitrogen gas at high temperature. How much silicon must react with excess nitrogen to prepare 125 g of silicon nitride if the yield of the reaction is 95.0%?



$$\% \text{ yield} = \frac{\text{actual}}{\text{theoretical}} = 95.0\% = \frac{125\text{g}}{x}$$

[5]

$$x = 139\text{g}$$

$$n_{\text{Si}_3\text{N}_4} = \frac{139\text{g}}{140.31\text{g/mol}} = 0.991$$

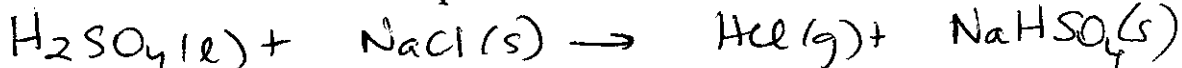


$$\therefore n_{\text{Si}} = 3n_{\text{Si}_3\text{N}_4} = 3(0.991) = 2.97\text{ mol}$$

$$m_{\text{Si}} = n \cdot \text{MM} = (2.97\text{ mol})(28.09\frac{\text{g}}{\text{mol}}) = \boxed{83.5\text{g}}$$

- (b) Liquid sulfuric acid reacts with solid sodium chloride to produce gaseous hydrogen chloride and sodium hydrogen sulfate solid.

- i) Write the balanced reaction for this process.



- ii) A 10.0 kg mass of NaCl reacts completely with sulfuric acid to give a certain volume of hydrogen chloride gas at 50. °C and 1.00 bar. If the same volume of hydrogen chloride gas is collected at 500. °C and 1.00 bar, what mass of NaCl has reacted?

$$\text{Since } n_{\text{NaCl}} = n_{\text{HCl}}$$

$$V = \frac{nRT}{P} = \frac{m}{\text{MM}} \frac{RT}{P} = \frac{(10.0 \times 10^3\text{g})(0.08314\frac{\text{bar}\cdot\text{L}}{\text{mol}\cdot\text{K}})(323\text{K})}{(58.44\frac{\text{g}}{\text{mol}})(1.00\text{ bar})} = 4,595\text{ L}$$

[5]

$$n = \frac{PV}{RT} = \frac{(1.00\text{ bar})(4,595\text{L})}{(0.08314\frac{\text{bar}\cdot\text{L}}{\text{mol}\cdot\text{K}})(773\text{K})} = 71.5\text{ mol}$$

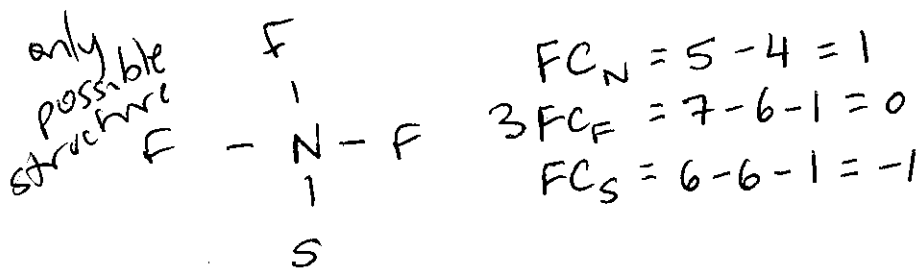
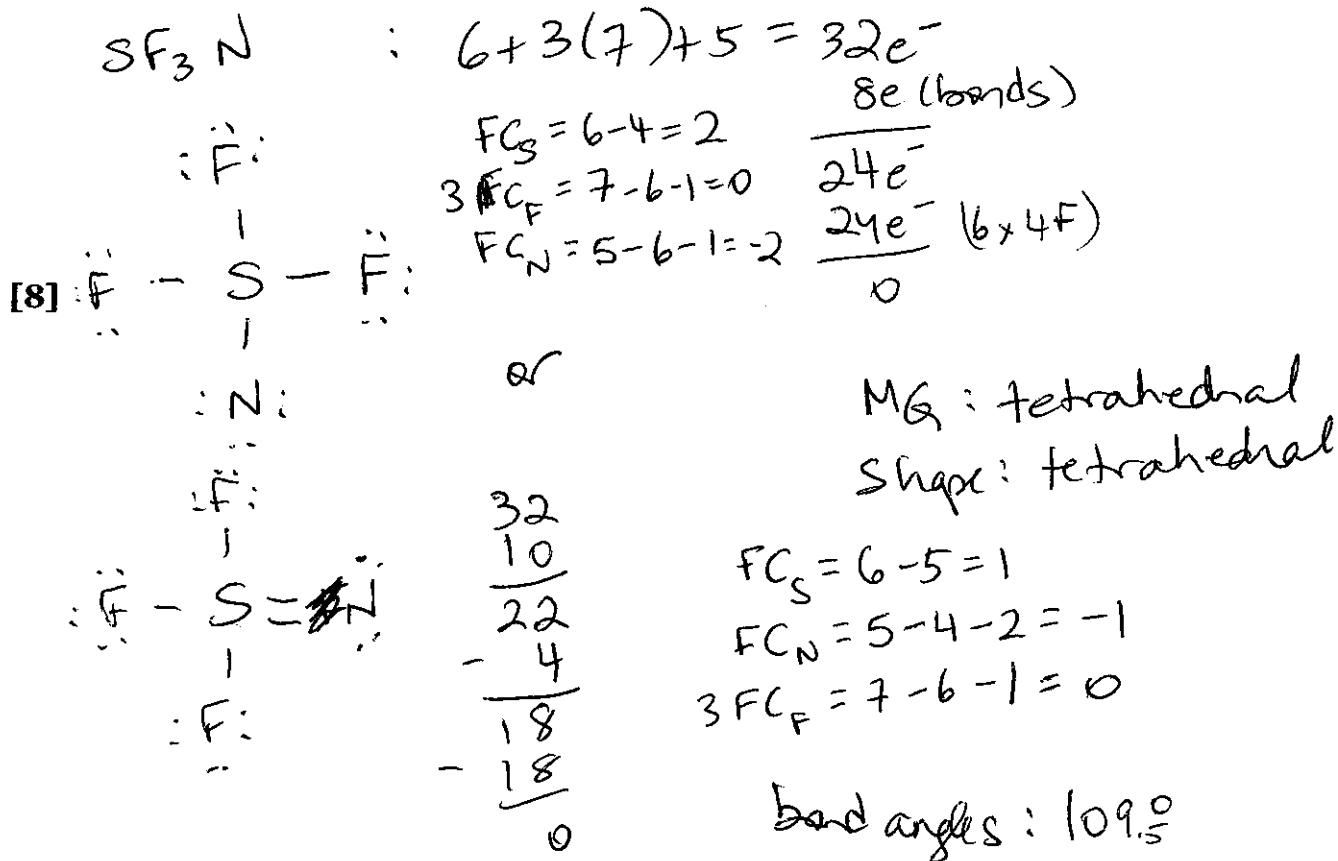
$$n_{\text{HCl}} = n_{\text{NaCl}}$$

$$\therefore m_{\text{NaCl}} = n \cdot \text{MM} = (71.5\text{ mol})(58.44\frac{\text{g}}{\text{mol}}) = \boxed{4.18\text{ kg}}$$

$$\begin{aligned} \text{NaCl:} \\ (22.99) + \\ 35.45 \\ = 58.44 \\ V = \frac{nRT}{P} \end{aligned}$$

(10) 3. The compound SF₃N has been synthesized.

- a) Draw the Lewis diagram of this molecule, supposing that the three fluoride atoms and the nitrogen atom surround the sulfur atom. Indicate the bond angles, the molecular geometry, the shape, and the formal charges on all atoms. Repeat the above assuming that the three fluorine atoms and the sulfur atom surround the nitrogen atom. Include ALL your work.



- (b) On the basis of the results of part (a), speculate about which arrangement is more likely to correspond to the actual molecular structure. Explain your answer.

[2]

Most likely S in the centre as it will take an expanded octet.
 But advantage to second structure is FC on N is (+) and S (-)

- (10) 4. (a) A mixture of aluminium and iron has a mass of 9.62 g. The mixture is reacted with aqueous HCl and the following parallel reactions (unbalanced) occur:



9.45 L of hydrogen gas was collected over water during the reaction at 1.016 bar and 29.8 °C when the metals reacted completely. What is the percent composition of the mixture (what mass percent Al and Fe)? The vapour pressure of water at 29.8 °C is 4.2455 kPa

[6]

$$P_{\text{H}_2} = 1.016 \text{ bar} - (4.2455 \text{ kPa}) \left(\frac{1 \text{ bar}}{10^2 \text{ kPa}} \right)$$

$$= 0.9735 \text{ bar}$$

$$n = \frac{PV}{RT} = \frac{(0.9735 \text{ bar})(9.45 \text{ L})}{(0.08314 \frac{\text{bar}\cdot\text{L}}{\text{mol}\cdot\text{K}})(29.8+273.2 \text{ K})} = 0.365 \text{ mol}$$

$$n_{\text{H}_2} = n_{\text{H}_2, \text{Fe}} + n_{\text{H}_2, \text{Al}}$$

$$0.365 \text{ mol} = n_{\text{Fe}} + \frac{3}{2} n_{\text{Al}} = \frac{m_{\text{Fe}}}{MM_{\text{Fe}}} + \frac{3}{2} \frac{m_{\text{Al}}}{MM_{\text{Al}}}$$

$$m_{\text{Fe}} + m_{\text{Al}} = 9.62$$

$$m_{\text{Fe}} = 9.62 - m_{\text{Al}}$$

$$\frac{9.62 - m_{\text{Al}}}{55.845} + \frac{3}{2} \frac{m_{\text{Al}}}{26.98} = 0.365$$

$$0.172 - 0.0179 m_{\text{Al}} + 0.0556 m_{\text{Al}} = 0.365$$

$$0.0377 m_{\text{Al}} = 0.193$$

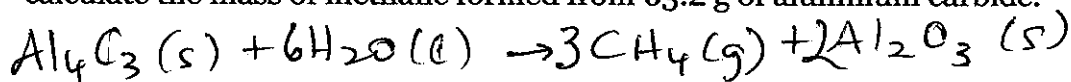
$$m_{\text{Al}} = 5.12 \text{ g}$$

$$\% \text{Al} = \frac{5.12}{9.62} \times 100\%$$

$$\% \text{Al} = 53.2\%$$

$$\% \text{Fe} = 46.8\%$$

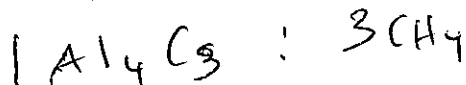
- (b) Solid aluminum carbide (Al_4C_3) reacts with water to produce gaseous methane and solid aluminum oxide. Write the balanced reaction and calculate the mass of methane formed from 63.2 g of aluminum carbide.



[4]

$$63.2 \text{ g}$$

$$n_{\text{Al}_4\text{C}_3} = \frac{m}{MM} = \frac{63.2 \text{ g}}{143.953 \frac{\text{g}}{\text{mol}}} = 0.439 \text{ mol}$$



$$\therefore n_{\text{CH}_4} = 3(0.439 \text{ mol}) = 1.317 \text{ mol}$$

$$m_{\text{CH}_4} = (1.317 \text{ mol}) \left(16.051 \frac{\text{g}}{\text{mol}} \right) = 21.1 \text{ g}$$

$$\begin{aligned} \text{Al}_4\text{C}_3 &= 4(26.98) + \\ & 3(12.011) \\ &= 143.953 \text{ g/mol} \end{aligned}$$

$$\begin{aligned} \text{CH}_4 &= 12.011 + 4(1.01) \\ &= 16.051 \text{ g/mol} \end{aligned}$$

- (10) 5. (a) In a study of the reaction of pyridine (C_5H_5N) with methyl iodide (CH_3I) in a benzene solution, the following set of initial rates was measured at $25^\circ C$ for different initial concentrations of the two reactants:

Experiment	$[C_5H_5N]_0$ (mol/L)	$[CH_3I]_0$ (mol/L)	Initial Rate (mol/L·s)
1	1.00×10^{-4}	1.00×10^{-4}	7.5×10^{-7}
2	2.00×10^{-4}	2.00×10^{-4}	3.0×10^{-6}
3	2.00×10^{-4}	4.00×10^{-4}	6.0×10^{-6}

- i) Determine the rate law expressed by this data.

using Expt 2 and 3 \Rightarrow double $[CH_3I]$, rate doubles
 $\therefore n = 1$

[4]

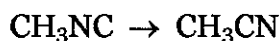
using Expt 1 and 2 $\Rightarrow [CH_3I]$ doubles so rate should double to $1.5 \times 10^{-6} \frac{\text{mol}}{\text{L}\cdot\text{s}}$
 Then double $[C_5H_5N] \Rightarrow$ rate doubles $\therefore m = 1$
 $\therefore \text{Rate} = k [C_5H_5N] [CH_3I]$

- ii) Calculate the rate constant with the CORRECT units.

$$7.5 \times 10^{-7} \frac{\text{mol}}{\text{L}\cdot\text{s}} = k (1.00 \times 10^{-4} \frac{\text{mol}}{\text{L}}) (1.00 \times 10^{-4} \frac{\text{mol}}{\text{L}})$$

$$k = 75 \frac{\text{L}}{\text{mol}\cdot\text{s}}$$

- b) The isomerization reaction



obeys the first-order rate law

$$\text{Rate} = -k [CH_3NC]$$

in the presence of an excess of argon. Measurements at 500 K reveal that in 520 s, the concentration of CH_3NC decreases to 71% of its original value.

- i) Calculate the rate constant k of the reaction at 500 K.

[1]

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

$$\ln \frac{0.71}{1} = -k(520\text{s})$$

$$k = 6.6 \times 10^{-4} \text{ s}^{-1}$$

- ii) What will the rate of the reaction be at this time if the initial concentration is 0.0735 mol/L?

[1]

$$\ln \frac{[A]_t}{[A]_0} = -kt \quad \ln \frac{[A]_t}{0.0735} = (-6.6 \times 10^{-4} \text{ s}^{-1}) \times 520$$

$$[A]_t = 0.052 \frac{\text{mol}}{\text{L}}$$

$$\text{Rate} = -k[\text{IClF}_3 \text{NC}] = -(6.6 \times 10^{-4} \text{ s}^{-1}) \left(0.052 \frac{\text{mol}}{\text{L}} \right) = -3.44 \times 10^{-5} \frac{\text{mol}}{\text{L s}}$$

- iii) The rate constant for the above reaction at 600 K is 0.41 s⁻¹. Calculate the activation energy for the reaction.

[2]

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{0.41}{6.6 \times 10^{-4}} = \frac{E_a}{8.314} \left(\frac{1}{500 \text{ K}} - \frac{1}{600 \text{ K}} \right)$$

$$E_a = 160.4 \frac{\text{kJ}}{\text{mol}}$$

- iv) Determine the frequency factor (pre-exponential factor, A) at 600 K.

[1]

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

$$A = \frac{k}{e^{-E_a/RT}} = \frac{0.41 \text{ s}^{-1}}{e^{-\frac{(160400 \text{ J/mol})}{(8.314)(600 \text{ K})}}} = 3.78 \times 10^{13} \text{ s}^{-1}$$

- v) Calculate the rate constant for this reaction at 1000 K.

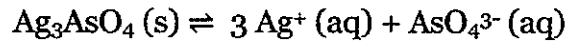
[1]

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{k_1}{0.41} = \frac{160400 \frac{\text{J}}{\text{mol}}}{8.314 \frac{\text{J}}{\text{mol K}}} \left(\frac{1}{600 \text{ K}} - \frac{1}{1000 \text{ K}} \right)$$

$$k_1 = 1.58 \times 10^5 \text{ s}^{-1}$$

- (10) 6. (i) Silver arsenate is a slightly soluble salt having $K_{sp} = 1.0 \times 10^{-22}$ at 25°C for the equilibrium



Calculate the molar solubility of silver arsenate in pure water at 25°C .

[5]

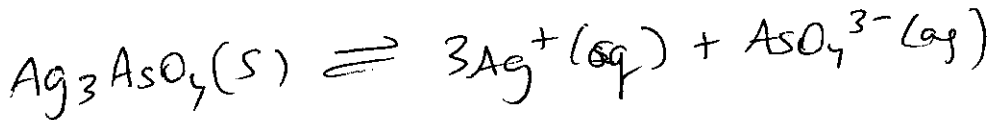
I	same	-	-
C	- S	3S	S
E	same	3S	S

$$K_{sp} = [\text{Ag}^+]^3 [\text{AsO}_4^{3-}] = (3S)^3 S = 27S^4 = 1.0 \times 10^{-22}$$

$$S = \boxed{1.4 \times 10^{-6} \frac{\text{mol}}{\text{L}}}$$

- (ii) Calculate the molar solubility of silver arsenate in $0.10 \text{ mol/L AgNO}_3$.

[5]



I	same	0.10	-
C	- S	3S	S
E	same	0.10 + 3S	S

$$K_{sp} = [\text{Ag}^+]^3 [\text{AsO}_4^{3-}] = (0.10 + 3S)^3 S = 1.0 \times 10^{-22}$$

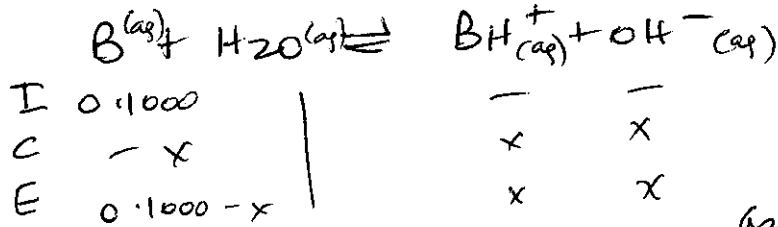
assume $3S \ll 0.10 \therefore 0.10 + 3S \approx 0.10$

$$(0.10)^3 S = 1.0 \times 10^{-22}$$

$$S = \boxed{1.0 \times 10^{-19} \frac{\text{mol}}{\text{L}}}$$

(12) 7. (a) Consider the titration of 40.00 mL of 0.1000 mol/L $(C_2H_5)_3NH_2$ (aq) with 0.1000 mol/L HCl (aq). (K_b for $(C_2H_5)_3NH_2$ (aq) is 6.41×10^{-4} at $25^\circ C$)

i) What is the original pH of the solution of $(C_2H_5)_3NH_2$ (aq)?



$$K_b = \frac{[BH^+][OH^-]}{[B]} = \frac{x^2}{0.1000 - x} = 6.41 \times 10^{-4}$$

assume $x \ll 0.1000$
 $\therefore 0.1000 - x \approx 0.1000$

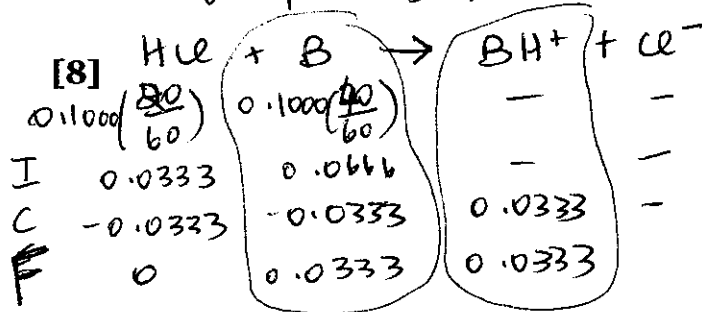
$$\frac{x^2}{0.1000} = 6.41 \times 10^{-4} \quad x = 8.00 \times 10^{-3} \frac{\text{mol}}{L}$$

$$\therefore pH = -\log[OH^-] = -\log(8.00 \times 10^{-3}) = 2.10$$

ii) What is the pH of the solution halfway through the titration?

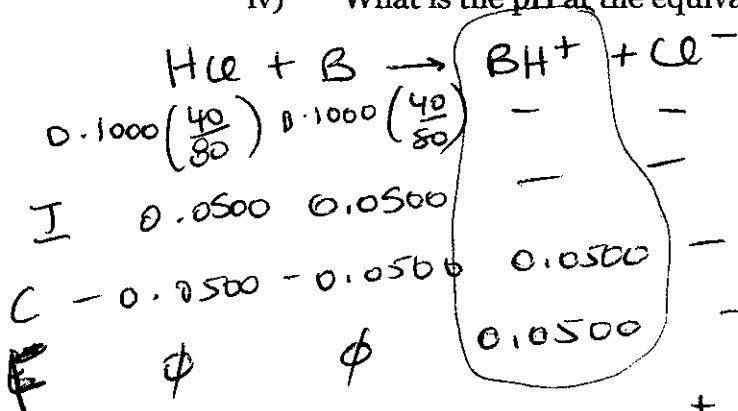
Halfway through, have added 20 mL HCl

$$\therefore pH = 14 - 2.10 = \boxed{11.90}$$



$$\begin{aligned} \therefore pH &= pK_a + \log \frac{[B]}{[BH^+]} \\ &= -\log \frac{K_w}{K_b} \\ &= -\log \left(\frac{1.0 \times 10^{-14}}{6.41 \times 10^{-4}} \right) \\ &= \boxed{10.81} \end{aligned}$$

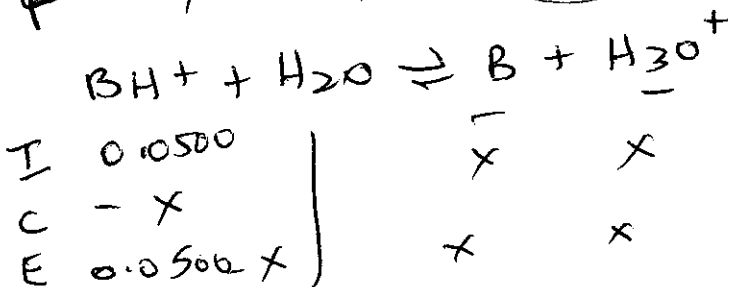
iv) What is the pH at the equivalence point?



$$K_a = \frac{[B][H_3O^+]}{[BH^+]} = \frac{x^2}{0.0500 - x}$$

$$1.56 \times 10^{-11} = \frac{x^2}{0.0500 - x}$$

assume $x \ll 0.0500$
 $0.0500 - x \approx 0.0500$
 Ok

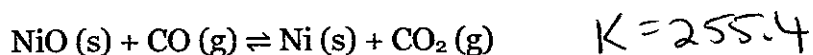


$$\frac{x^2}{0.0500} = 1.56 \times 10^{-11}$$

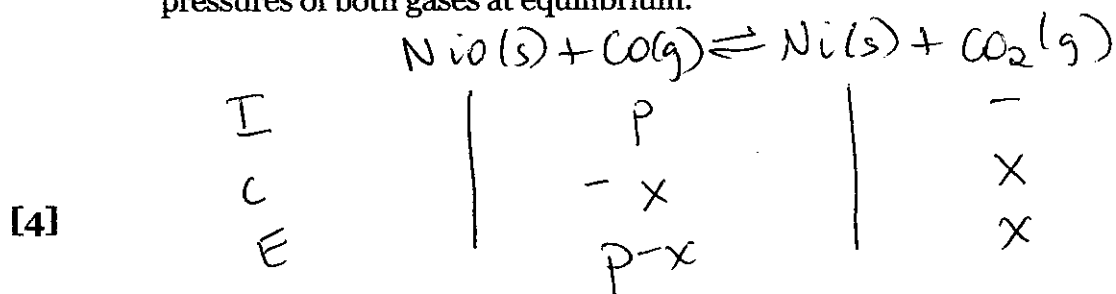
$$x = 8.83 \times 10^{-7} \frac{\text{mol}}{L} = [H_3O^+]$$

$$\therefore pH = -\log(8.83 \times 10^{-7}) = \boxed{6.05}$$

- (8) 8. The equilibrium constant for the reduction of nickel(II)oxide to nickel at 754°C is 255.4, corresponding to the reaction



If the total pressure of the system at 754°C is 2.50 bar, calculate the partial pressures of both gases at equilibrium.



$$p - x + x = p = 2.50 \text{ bar}$$

$$K = \frac{P_{\text{CO}_2}}{P_{\text{CO}}} = \frac{x}{2.50 - x} = 255.4$$

$$x = 255.4(2.50 - x)$$

$$= 638.5 - 255.4x$$

$$256.4x = 638.5$$

$$\therefore \boxed{P_{\text{CO}} = 0.01 \text{ bar} \quad P_{\text{CO}_2} = 2.49 \text{ bar}} \quad x = 2.49 \text{ bar}$$

- (b) You have a supply of ice at 0.0°C and a glass containing 150 g of water at 25°C . The enthalpy of fusion for ice is $\Delta_{\text{fus}}H^{\circ} = 333 \text{ J/g}$ and the specific heat capacity of water is $4.18 \text{ J/g}\cdot^{\circ}\text{C}$. What mass of ice must be added to the glass and melted to reduce the temperature of the water to 0.0°C ?

[4]

$$-q_{\text{H}_2\text{O}} = q_{\text{ice}}$$

$$-(mc\Delta T)_{\text{H}_2\text{O}} = (\Delta H^{\circ}_{\text{fus}} \cdot m)_{\text{ice}}$$

$$-(150 \text{ g}) \left(4.18 \frac{\text{J}}{\text{g}\cdot^{\circ}\text{C}} \right) (0 - 25^{\circ}\text{C}) = \left(333 \frac{\text{J}}{\text{g}} \right) (m)$$

$$\boxed{m_{\text{ice}} = 47 \text{ g}}$$

- (10) 9. Dianabol is one of the anabolic steroids that has been used by some athletes to increase the size and strength of their muscles. It is similar to the male hormone testosterone. Some studies indicate that the desired effects of the drug are minimal, and the side effects, which include sterility and increased risk of liver cancer and heart disease, keep most people from using it. The molecular formula of Dianabol, which consists of carbon, hydrogen, and oxygen, can be determined using the data from two different experiments. In the first experiment, 14.765 g of Dianabol is burned, and 43.257 g CO₂ and 12.395 g H₂O are formed. In the second experiment, the molecular mass of Dianabol is found to be 300.44 g/mol. What is the molecular formula for Dianabol?

$$n_c = n_{\text{CO}_2} = \frac{m}{\text{MM}} = \frac{43.257 \text{ g}}{44.01 \frac{\text{g}}{\text{mol}}} = 0.9829 \text{ mol}$$

$$m_c = n_c \cdot \text{MM}_c = \left(12.011 \frac{\text{g}}{\text{mol}}\right) (0.9829 \text{ mol}) = \underline{11.80 \text{ g}}$$

$$n_{\text{H}_2\text{O}} = \frac{m_{\text{H}_2\text{O}}}{\text{MM}_{\text{H}_2\text{O}}} = \frac{12.395 \text{ g}}{18.02 \frac{\text{g}}{\text{mol}}} = 0.6878 \text{ mol}$$

$$n_{\text{H}} = 2n_{\text{H}_2\text{O}} = 2(0.6878 \text{ mol}) = \underline{1.3757 \text{ mol}}$$

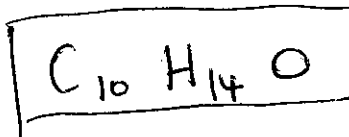
$$m_{\text{H}} = n_{\text{H}} \cdot \text{MM}_{\text{H}} = \left(1.00794 \frac{\text{g}}{\text{mol}}\right) (1.3757 \text{ mol}) = \underline{1.3866 \text{ g}}$$

$$m_o = m_{\text{samp}} - m_c - m_{\text{H}} = 14.765 \text{ g} - 11.80 \text{ g} - 1.3866 \text{ g} = \underline{1.5789 \text{ g}}$$

$$n_o = \frac{m_o}{\text{MM}_o} = \frac{1.5789 \text{ g}}{15.9994 \frac{\text{g}}{\text{mol}}} = 0.09865 \text{ mol}$$

∴ empirical formula is

$$\text{C} \frac{0.9829}{0.09865} \quad \text{H} \frac{1.3757}{0.09865} \quad \text{O} \frac{0.09865}{0.09865}$$



$$\text{MM}_{\text{emp}} = (10) \left(12.011 \frac{\text{g}}{\text{mol}}\right) + (14) \left(1.00794 \frac{\text{g}}{\text{mol}}\right) + (1) \left(15.9994 \frac{\text{g}}{\text{mol}}\right) = 150.22 \frac{\text{g}}{\text{mol}}$$

$$\# \text{ units} = \frac{\text{MM}}{\text{MM}_{\text{emp}}} = \frac{300.44 \frac{\text{g}}{\text{mol}}}{150.22 \frac{\text{g}}{\text{mol}}} = 2$$

$$\therefore \text{molecular formula is : } \boxed{\text{C}_{20} \text{H}_{28} \text{O}_2}$$