

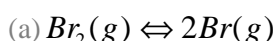
Exercises Topic 5: Equilibrium reactions

1. Considering the values of K_p for the chemical dissociation of molecular bromine in atomic bromine as a function of temperature shown in Table 1, determine: a) ΔG° , ΔH° and ΔS° for this reaction and b) K_c at 1500 K. Assume that ΔH° and ΔS° are constant throughout this temperature range.

Table 1

K_p	0.05	0.12	0.25
T (K)	1400	1500	1600

Solution

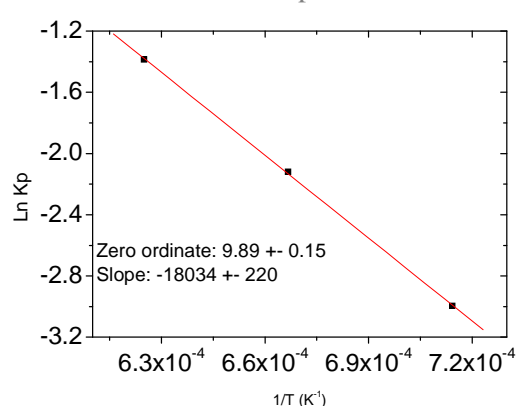


$$\Delta G^0 = -RT \cdot \ln K_p;$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

$$\ln K_p = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R} \cdot \frac{1}{T} \Rightarrow \text{Plotting } \ln K_p \text{ vs } 1/T \text{ (K}^{-1}\text{) it should yield a straight line of}$$

which zero ordinate it is possible to calculate ΔS^0 and of its slope $-\Delta H^0/R$.



Therefore:

$$\ln K_p = 9.89 - 18034 \cdot \frac{1}{T};$$

Then: $\Delta S^0 = 82.2 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ and $\Delta H^0 = +149.97 \text{ kJ} \cdot \text{mol}^{-1}$.

And

$$\Delta G^0 (1400) = 149970 - 1400 \cdot 82.2 = 35.9 \text{ kJ} \cdot \text{mol}^{-1}$$

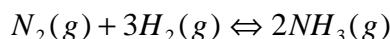
$$\Delta G^0 (1500) = 149970 - 1500 \cdot 82.2 = 26.7 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta G^0 (1600) = 149970 - 1600 \cdot 82.2 = 18.5 \text{ kJ} \cdot \text{mol}^{-1}$$

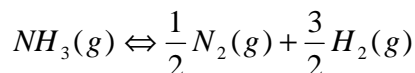
(b) $K_p = K_c \cdot (RT)^{\Delta n} \Rightarrow K_c = \frac{K_p}{(RT)^{\Delta n}} = K_p (RT)^{-\Delta n}$; Since $\Delta n = 1$, therefore

$$K_c = \frac{K_p}{(RT)^1} = K_p (RT)^{-1}; K_c = \frac{0.12}{(0.082 \cdot 1500)} = 49.75 \cdot 10^{-4}$$

2. The equilibrium constant at 298.15 K for the synthesis of ammonia from its elements is $K_p = 3.6 \cdot 10^8$.



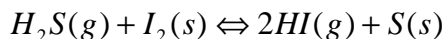
What is the value of K_p at 298.15 K for the following reaction?



Solution: The equilibrium constant for the direct reaction K_p is: $K_p = \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3}$; and for the reverse reaction K_p' , is

$$K_p' = \frac{P_{H_2}^{3/2} P_{N_2}^{1/2}}{P_{NH_3}} = \frac{1}{\frac{P_{H_2}^{3/2} P_{N_2}^{1/2}}{P_{NH_3}}} = \frac{1}{\left(\frac{P_{H_2}^3 P_{N_2}}{P_{NH_3}^2} \right)^{1/2}} = \frac{1}{K_p^{1/2}} = \frac{1}{(3.6 \cdot 10^8)^{1/2}} = 5.27 \cdot 10^{-5}$$

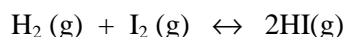
3. At equilibrium in the following reaction at 50 °C, the partial pressures of the gases are found to be $P(\text{HI}) = 3.65 \cdot 10^{-3}$ atm and $P(\text{H}_2\text{S}) = 9.96 \cdot 10^{-1}$ atm. What is the value of K_p ?



Solution: The equilibrium constant in terms of activities is given by $K_p = \frac{a(\text{S}) \cdot a(\text{HI})^2}{a(\text{I}_2) \cdot a(\text{H}_2\text{S})}$. Since the activities of pure liquids and pure solids is 1, the equilibrium constant can be written as

$$K_p = \frac{a(\text{HI})^2}{a(\text{H}_2\text{S})} = \frac{P(\text{HI})^2}{P(\text{H}_2\text{S})} = \frac{(3.65 \cdot 10^{-3})^2}{9.96 \cdot 10^{-1}} = 1.34 \cdot 10^{-5}$$

4. A gaseous mixture containing 0.05 moles of H_2 and 0.039 moles of I_2 is prepared at 300 °C. The equilibrium mixture is found to contain 0.068 moles of HI. Calculate: a) the equilibrium constants K_c and K_p ; b) the net change in free energy (ΔG°) of this reaction.

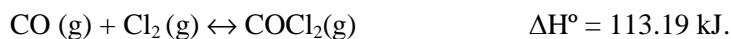


Solution: (a) $K_c = K_p = 57.8$; b) $\Delta G^\circ = -19.32$ kJ/mol

5. Starting with 0.1 moles of $\text{AsCl}_5(\text{g})$ in a 1-L flask, the system is heat up to 182 °C and when equilibrium is established 0.087 moles of AsCl_5 are present. Consider the dissociation reaction of AsCl_5 into AsCl_3 and chlorine and determine: a) the numerical values of K_p and K_c and b) the concentrations of the different gases if the volume is raised from 1 to 3 litres, at the same temperature.

Solution: (a) $K_c = 1.93 \cdot 10^{-3}$; $K_p = 0.07245$; (b) Equilibrium constant only depends on temperature. $[\text{AsCl}_3] = 4.33 \cdot 10^{-3}$ mol/L; $[\text{AsCl}_5] = 0.029$ mol/L

6. Consider the following reaction:



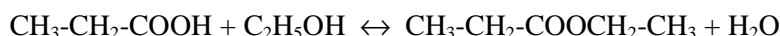
Predict how each of the following factors affects the chemical equilibrium: (a) Introduce 1 mole of chlorine at constant volume. (b) Double the volume of the flask at constant temperature. (c) Introduce one mole of a noble gas at constant volume and temperature. (d) The temperature is raised at constant pressure. (e) The pressure is raised at constant temperature.

Solution: (a) \rightarrow ; (b) \leftarrow ; (c) No effect; (d) \leftarrow ; (e) \rightarrow

7. 5 g of $\text{SbCl}_5(\text{s})$ are introduced in a 1-L flask and hermetically closed. The temperature is raised at 200 °C causing the complete sublimation of SbCl_5 . The final pressure is 1 atm. Also it is well known that the PCl_5 can dissociate according to the following reaction $\text{SbCl}_5(\text{g}) \rightleftharpoons \text{SbCl}_3(\text{g}) + \text{Cl}_2(\text{g})$. Explain whether the dissociation of the PCl_5 takes place or not. **Data:** $M(\text{Sb}) = 121.76 \text{ g} \cdot \text{mol}^{-1}$; $M(\text{Cl}) = 35.45 \text{ g} \cdot \text{mol}^{-1}$.

Solution: The dissociation of SbCl_5 will not take place since $K_p < 1$ and $\Delta G > 0$

8. Propanoic acid reacts with ethanol yielding ethyl propionate and water according to the following reaction:



At 35 °C K_c is 4. At this temperature, calculate: a) the numeric value of moles of ethyl propionate formed if initially a mixture of 3.2 moles of propanoic acid and 2 moles of ethanol is prepared; b) the amount of ethyl propionate (in grams) that will be obtained mixing 105 g of ethanol with 150 g of propanoic acid when the equilibrium is established.

Data: $M(\text{CH}_3\text{-COOH}) = 74 \text{ g/mol}$; $M(\text{C}_2\text{H}_5\text{OH}) = 42 \text{ g/mol}$; $M(\text{CH}_3\text{-COOCH}_2\text{-CH}_3) = 102 \text{ g/mol}$.

Solution: (a) 1.6 moles; (b) 29.5 g

9. For the reaction: $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$, at 1573 K, 63 % of an equimolecular mixture of CO_2 and H_2 is transformed into CO and H_2O . Calculate: a) K_p and ΔG° at 1573 K and b) ΔH° y ΔS° for this reaction. Assume ΔH° and ΔS° to be constant within the range of temperatures considered.

	$\text{CO}_2(\text{g})$	$\text{H}_2(\text{g})$	$\text{CO}(\text{g})$	$\text{H}_2\text{O}(\text{g})$
ΔG_f° at 25°C (kcal mol ⁻¹)	-94.7	0	-31.8	-54.9

Solution: (a) $K_p(1573 \text{ K}) = 2.899$; $\Delta G^\circ(1573 \text{ K}) = -13.92 \text{ kJ/mol}$; (b) $K_p(298 \text{ K}) = 1.36 \cdot 10^{-6}$; $\Delta G^\circ(298 \text{ K}) = 33.47 \text{ kJ/mol}$; $\Delta S^\circ = 37.17 \text{ J/mol}$; $\Delta H^\circ = 44.5 \text{ kJ/mol}$

10. For the reaction: $\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{CO}_2(\text{g})$, the equilibrium constant is 5.1 at 800 K. If a gaseous mixture of 1 mol each of CO and H_2O is heat up to 800 K in a 50-L container, calculate: (a) The moles of CO present in the reaction mixture once the equilibrium is established. (b) The partial pressure of each gas as well as the total pressure in the vessel. (c) If two moles of water are added how many moles of CO would be present in the container when the equilibrium is re-established?

Solution: (a) 0.307 moles of CO ; (b) $P(\text{CO}) = P(\text{H}_2\text{O}) = 0.402 \text{ atm}$; $P(\text{H}_2) = P(\text{CO}_2) = 0.909 \text{ atm}$; (c) 0.08 moles of CO

11. For a 0.2 M sodium acetate aqueous solution calculate the pH and the concentrations of all the species present at the equilibrium

Data: $K_a(\text{HAc}) = 10^{-4.75}$.

Solution: $[\text{Ac}^-] = 0.1999 \approx 0.2 \text{ M}$; $[\text{AcH}] = 1.065 \cdot 10^{-5} \text{ M}$; $[\text{OH}^-] = 1.065 \cdot 10^{-5} \text{ M}$; $\text{pH} = 9.02$

12. Calculate the pH of the solutions resulting from the mixture of: a) 10 mL de NaOH 0.1M and 5 mL de HCl 0.1M; b) 20 mL de NaOH 0.1M and 20 mL de HCl 0.1M; c) 10 mL de NaOH 0.1M and 25 mL of HCl 0.1M.

Solution: NaOH and HCl are strong electrolytes so they are completely dissociated. The corresponding ions are monovalent so number of moles and number of equivalents coincide. For solving, we first calculate the number of moles involved for a given mixture and then we consider the final concentration taking into account the final volume and assuming that the volumes are additive.

a) The initial number of moles, expressed in mmoles (1 mmoles = $1 \cdot 10^{-3}$ moles):

$$\text{mmoles of NaOH: } 10 \text{ mL} \cdot (10^{-3} \text{ L/mL}) \times 0.1 \text{ mol} \cdot \text{L}^{-1} = 10^{-3} \text{ mol} = 1 \text{ mmol}$$

$$\text{mmoles of HCl: } 5 \times 0.1 = 0.5 \text{ mmol}$$

$$V_{\text{total}}(\text{ml}) = 10 + 5 = 15 \text{ mL}$$

When NaOH and HCl are mixed the following neutralization reaction takes place:

	HCl	+	NaOH	\rightleftharpoons	Cl^-	+	Na^+	+	H_2O
mmoles _{initial}	0.5		1		--				--
mmoles _{changes}	-0.5		-0.5		0.5		0.5		0.5
mmoles _{final}	--		0.5		0.5		0.5		0.5

Neither Cl^- nor Na^+ hydrolyzes. Therefore, the pH is given by:

	NaOH	+	H_2O	\rightleftharpoons	Na^+	+	OH^-
mmoles _{initial}	0.5				--		
mmoles _{final}	---		---		0.5		0.5

$$\text{mmoles de OH}^- = 0.5 \Rightarrow [\text{OH}^-] = 0.5/15 = 0.0333 \text{ M} \Rightarrow$$

$$\text{pOH} = -\log [\text{OH}^-] = 1.47 \Rightarrow \text{pH} = 12.52$$

b) Following the same approach than in (a), we have:

$$\text{mmoles of NaOH: } 20 \times 0.1 = 2 \text{ mmol}$$

$$\text{mmoles of HCl: } 20 \times 0.1 = 2 \text{ mmol}$$

$$V_{\text{total}} (\text{ml}) = 20 + 20 = 40 \text{ mL}$$

A strong acid (HCl) reacts with a strong base (NaOH) yielding a neutralization reaction:

	HCl	+	NaOH	\Leftrightarrow	Cl⁻	+	Na⁺	+	H₂O
mmoles _{iniciales}	2		2		--				--
mmoles _{changes}	-2		-2		2		2		2
mmoles _{final}	--		---		2		2		x

Neither Cl⁻ nor Na⁺ hydrolyzes. Therefore, the pH is given by the self-ionization of water:

	H₂O	\Leftrightarrow	OH⁻	+	H₃O⁺
mmoles _{initial}			--		
mmoles _{changes}			x		2
mmoles _{final}	---		x		x

$$K_w(\text{H}_2\text{O}) = 10^{-14} = [\text{OH}^-] \times [\text{H}_3\text{O}^+] = (x) \cdot (x) \Rightarrow x = [\text{H}_3\text{O}^+] = \sqrt{K_w} = 10^{-7} \text{ M} \Rightarrow \text{pH} = 7$$

c) Initially we have:

$$\text{mmoles of NaOH: } 10 \times 0.1 = 1 \text{ mmol}$$

$$\text{mmoles of HCl: } 25 \times 0.1 = 2.5 \text{ mmol}$$

$$V_{\text{total}} (\text{ml}) = 10 + 25 = 35 \text{ mL}$$

	HCl	+	NaOH	\Leftrightarrow	Cl⁻	+	Na⁺	+	H₂O
mmoles _{initial}	2.5		1		--				--
mmoles _{changes}	-1		-1		1		1		1
mmoles _{final}	1.5		---		1		1		1

Here, pH is given by:

	HCl	+	H₂O	\Leftrightarrow	Cl⁻	+	H₃O⁺
mmoles _{initial}	1.5				--		
mmoles _{final}	---		---		1.5		1.5

$$\text{mmoles of H}_3\text{O}^+ = 1.5 \Rightarrow [\text{H}_3\text{O}^+] = 1.5/35 = 0.043 \text{ M} \Rightarrow \text{pH} = -\log[\text{H}_3\text{O}^+] = 1.37$$

13. Calculate the pH of each of the following solutions: a) 60 mL of a 0.5 M NH₃ solution. b) The resulting solution if 30 mL of HCl 0.5 M are added to the solution in (a).

DATA: pK_b(NH₃) = 4.8

Solution: a) Considering the following equilibrium for ammonia in an aqueous solution:

	NH₃	+	H₂O	\Leftrightarrow	NH₄⁺	+	OH⁻
C _{initial}	0.5				--		--
C _{final}	0.5-x				x		x

$$K_b(\text{NH}_3) = \frac{[\text{NH}_4^+] \cdot [\text{OH}^-]}{[\text{NH}_3]} = \frac{x^2}{(0.5-x)} \approx \frac{x^2}{0.5} \Rightarrow x = \sqrt{0.5 \cdot K_b} = 2.82 \cdot 10^{-3} \Rightarrow$$

$$\text{pOH} = 2.55 \Rightarrow \text{pH} = 11.45$$

b) Assuming that volumes are additive, first we recalculate the initial concentrations of each of the species. The new concentrations can be calculated as follows:

$$[NH_3] = \frac{[NH_3]_0 \times V_0}{V_f} = \frac{0.5 \times 60}{80} = 0.375 M$$

$$[HCl] = \frac{[HCl]_0 \times V_0}{V_f} = \frac{0.5 \times 30}{80} = 0.1875 M$$

Consider the following neutralization reaction:

	NH ₃	+	HCl	⇌	NH ₄ ⁺	+	Cl ⁻
C _{initial}	0.375		0.1875		--		--
C _{changes}	-0.1875		-0.1875		0.1875		0.1875
C _{final}	0.1875		---		0.1875		0.1875

Note that ammonia is in excess with respect to HCl. After neutralization, a buffer solution is formed (weak base/conjugate acid - [NH₃]/[NH₄⁺]). Both species are in equilibrium so we can write

	NH ₃	+	H ₂ O	⇌	NH ₄ ⁺	+	OH ⁻
C _{initial}	0.1875				0.1875		--
C _{changes}	-x		-x		x		x
C _{final}	0.1875-x		---		0.1875+x		x

$$K_b(NH_3) = 10^{-4.8} = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(0.1875+x) \cdot x}{0.1875-x} \approx \frac{0.1875 \cdot x}{0.1875} \Leftrightarrow x = [OH^-] = 1.8 \times 10^{-5} M \Rightarrow$$

$$pOH = 4.74 \Rightarrow pH = 9.26$$

14. Calculate the percent ionization of hydrofluoric acid at the following concentrations: a) 0.50 M; b) 0.003 M and c) $2.1 \cdot 10^{-4}$ M and comment on the trends. **Data:** pK (HF) = 3.18.

Solution: (a) 3.57 %; b) 37.19 %; (c) 79.77 %

15. Determine the titration curve of a 100 mL 0.1 M acetic acid solution with a 0.1 M NaOH solution.

Hint: Use a worksheet to calculate pH every 5 mL of added NaOH; calculate pH for three additions after the equivalence point. Plot the results using the graphical tools of the worksheet .

Data pK(HAc) = 4.75

Solution: (a) Before NaOH, pH = 2.87; (b) After addition 95 mL NaOH, pH = 6.02; (c) At the equivalence point, when 100 mL of NaOH are added, pH = 8.02; (d) After addition 105 mL NaOH, pH = 11

16. Consider a solution that is 0.15 M in acetic acid (CH₃COOH) and 0.5 M in hydrochloric acid (HCl), calculate: a) the concentration of acetate ions; b) the concentration of non-ionized acid (HAc) and c) the pH of the solution.

Data: K_a(CH₃COOH) = $1.8 \cdot 10^{-5}$.

Solution: (a) [Ac⁻] = $5.4 \cdot 10^{-6}$ M; (b) [AcH] ≈ 0.15 M; (c) pH = 0.3

17. Given a 0.2 M NH₄Cl solution: (a) What is the pH of this solution? (b) If 100 mL of 0.1 M HCl solution are added to 100 mL of the original solution, what is the pH? (c) And if 100 mL of 0.1 M NH₃ are added to 100 mL of the original solution?

Data: K_b(NH₃) = $1.8 \cdot 10^{-5}$.

Solution: (a) pH = 4.98; (b) pH = 1.3; (c) pH = 8.95

18. Given the following buffer solution containing both 0.1 M each HAc and NaAc, determine: a) the pH and b) the change in pH after adding 50 mL of water to 50 mL of the buffer solution.

Data: K_a (HAc) = $1.8 \cdot 10^{-5}$.

Solution: pH = 4.74. pH does not change appreciably with dilution.

19. You need to prepare 2 L of a phosphate buffer solution at pH = 7. How many grams of sodium hydrogen phosphate and dihydrogen phosphate should you weight?

Data: The pK values of phosphoric acids can be taken from the transparencies.

Solution: mass (Na₂HPO₄) = 283.94 g; mass (NaH₂PO₄) = 38.7 g

20. Calculate the pH interval in which a change of colour will be observed for the two following indicators: methyl orange (pK = 3.4) and phenolphthalein (pK = 9.4).

Solution: pH = pK_a - 1 acid form; pH = pK_a + 1 basic form; methyl orange 3.4 ± 1; phenolphthalein 9.4 ± 1

21. Determine the concentration of ammonia that will be suitable for the precipitation of Fe(OH)₂ from a solution that is initially 0.005M in FeBr₂.

Data: K_s(Fe(OH)₂) = 1.6 · 10⁻¹⁰; K_b(NH₃) = 1.8 · 10⁻⁵.

Solution: [NH₃] = 1.96 · 10⁻³ M

22. To a solution that is 0.01 M in Cl⁻ and Br⁻ is slowly added AgNO₃ (aq). Determine: a) which anion should precipitate first; b) what is the [Ag⁺] concentration at the point at which the second anion begins to precipitate? c) Can the Cl⁻ and Br⁻ be separated effectively by this fractional precipitation?

Data: K_s(AgBr) = 7.7 · 10⁻¹³; K_s(AgCl) = 1.6 · 10⁻¹⁰.

Solution: (a) AgBr will precipitate first; (b) Cl⁻ will begin to precipitate when [Ag⁺] = 1.6 · 10⁻⁸ M; (c) The initial concentration of Br⁻ is 0.01 M; The final concentration of Br⁻ before Cl⁻ begins to precipitate is 4.81 · 10⁻⁵. The yield of the separation will be 99.5 %

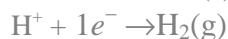
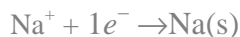
23. Compare the molar solubility of Mg(OH)₂ in water and in a solution buffered at a pH of 8.5. **Data:** K_s (Mg(OH)₂) = 1.2 · 10⁻¹¹.

Solution: In water, solubility is 1.44 · 10⁻⁴ M and at pH = 8.5, solubility is 1.2 M. But pH = 8.5 is lower than the natural pH Mg(OH)₂ solutions, which is 10.46.

24. An aqueous 0.5M Na₂SO₄ solution is electrolyzed: (a) Write the oxidation and reduction half-reactions. (b) What will be the volume of H₂ and O₂ produced if a 4 A current is passed through the circuit for 45 minutes and the gases are collected at 740 mmHg and 27°C? Assume that the current efficiency is 100%. (c) If the total voltage of the cell is 5 V, what is the energy consumption is kW/h per m³ of generated H₂?

Solution: a) When you hydrolyze a water solution the positive electrode will be the anode and the negative electrode will be the cathode. Electrons enter the water at the cathode giving rise to reduction reactions. Cations, because of their positive charge tend to concentrate in the cathode and anions in the anode. Therefore, cations will tend to reduce and anions to oxidize.

Which are the possible reduction processes that can take place at the cathode is the first question to analyze for a proper experiment design. These are the reduction of Na⁺ cations and the reduction of H⁺ cations according to:



Obviously, SO₄²⁻ anions are also susceptible to be reduced but because of their negative charge they accumulate in the anode so this reduction process will not take place. The reduction potential for Na⁺ is -2.714 V; this is a very large negative value that clearly indicates that this reduction process is thermodynamically very unfavorable. Therefore, if there are any other species with a lower reduction potential they will reduce before. Water can be reduced according to:

H⁺ + 1e⁻ → H₂(g), which has a zero potential in standard conditions

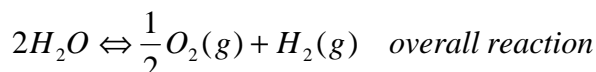
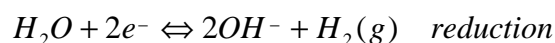
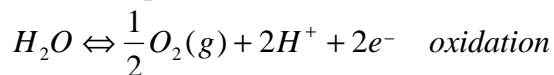
2H₂O + 2e⁻ → H₂(g) + 2OH⁻, which has a reduction potential of -0.828 V.

Since sulphate anion is the conjugate base of hydrogensulphate acid, a relatively strong acid, hydrolysis of sulphate can be disregarded. Therefore, pH is almost 7 so the preferred reduction will be

the second one. At the anode the oxidation that takes place must be the oxidation of water since sulfur in the sulphate anion is in its highest oxidation state. The reaction is



Therefore, the two reactions that take place are:



The potential that must be applied for the electrolysis to occur will be $-1.229 + (-0.828) = 2.06 \text{ V}$.

b) To obtain $\frac{1}{2}$ mol of O_2 and 1 mol of H_2 we need 2 moles of e^- . A current of 4 A is equivalent to a charge of 4 Coulombs per second. Taking into account that the charge of 1 mol of electrons is 96500 coulombs, the number of moles of hydrogen and oxygen that are produced is:

$$n_{\text{H}_2} = 4 \times 45 \times 60 \times \frac{1}{96500} = 5.595 \cdot 10^{-2} \text{ mol}$$

$$n_{\text{O}_2} = \frac{n_{\text{H}_2}}{2} = 2.798 \cdot 10^{-2} \text{ mol}$$

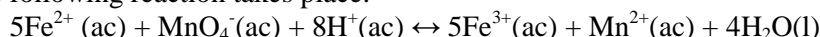
Assuming ideal gas behavior, the volume occupied by these two gases will be:

$$V_{\text{H}_2} = \frac{n_{\text{H}_2} RT}{P} = \frac{5.595 \cdot 10^{-2} \cdot 0.082 \cdot 300}{\frac{740}{760}} = 1.413 \text{ L}$$

$$V_{\text{O}_2} = \frac{n_{\text{O}_2} RT}{P} = \frac{2.798 \cdot 10^{-2} \cdot 0.082 \cdot 300}{\frac{740}{760}} = 0.707 \text{ L}$$

c) The consumed energy in joules is $E = 4 \times 30 \times 60 \times 5 = 36\,000 \text{ J}$. But since 1Kw-h is equivalent to $3.6 \cdot 10^6 \text{ J}$, the energy in Kw-h will be 0.011 Kw-h. This quantity divided by the volume of H_2 gives $7.78 \text{ Hw-h/m}^3(\text{H}_2)$.

25. A cell where the following reaction takes place:



can be built in the following way: a platinum electrode is introduced in a container containing a solution of potassium permanganate and sulfuric acid. Another platinum electrode is introduced in a second container that contains a solution of iron sulfate. A saline bridge is used to connect the two containers, and the electrodes are connected to a voltmeter. (a) What is the standard potential of the cell? (B) What reaction takes place in the anode and the cathode? What is the direction of electron movement through the external circuit? (c) What is the equilibrium constant of the reaction at $25 \text{ }^\circ\text{C}$? (d) What can you conclude from the value of the equilibrium constant?

Data: $E^0(\text{MnO}_4^-/\text{Mn}^{2+}) = 1.512 \text{ V}$; $E^0(\text{Fe}^{3+}/\text{Fe}^{2+}) = 0.771 \text{ V}$

Solution: First we need to recognize which species are reducing and which are oxidizing. Fe^{2+} oxidizes into Fe^{3+} and MnO_4^- reduces to Mn^{2+} . So we must turn the reduction potential of Fe^{3+} . The cell potential will be $E^0(\text{MnO}_4^-/\text{Mn}^{2+}) - E^0(\text{Fe}^{3+}/\text{Fe}^{2+}) = 1.512 - 0.771 = 0.739 \text{ V}$.

Fe^{2+} oxidizes into Fe^{3+} in the anode and MnO_4^- reduces to Mn^{2+} in the cathode. Electrons are produced in the anode and move to the cathode.

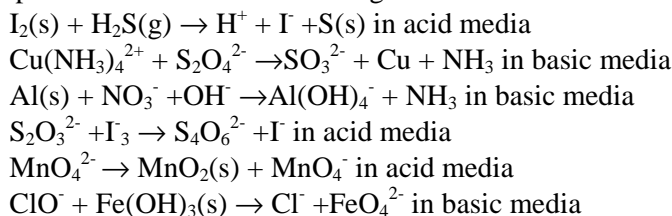
The equilibrium constant of the redox reaction is given by

$$E = E^0 - \frac{0.0257}{n} \ln Q = E^0 - \frac{0.059}{5} \log Q \quad \textit{at equilibrium } E = 0 \text{ and } Q = K$$

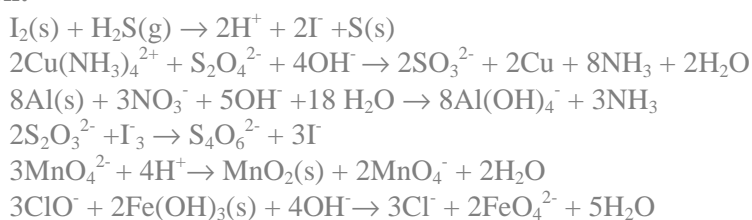
$$K = 10^{\frac{E^0 n}{0.059}} = 10^{\frac{0.739 \times 5}{0.059}} = 4.24 \cdot 10^{62}$$

The redox reaction is totally displaced through the right.

26. Complete and balance the following redox reactions:



Solution:



27. Balance the following redox processes and explain whether they are spontaneous processes or not. Assume standard conditions: (a) Oxidation metallic silver in an acid aqueous solution. (b) Oxidation metallic silver in an basic aqueous solution

Data: $E^0(\text{Ag}^+/\text{Ag}) = +0.80 \text{ V}$; $E^0(\text{O}_2/\text{OH}^-) = +0.40 \text{ V}$

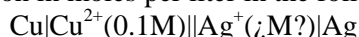
Solution: (a) $2\text{Ag}(\text{s}) + 2\text{H}^+(\text{ac}) \rightarrow 2\text{Ag}^+(\text{ac}) + \text{H}_2(\text{g})$; $E < 0$, non spontaneous; (b) $4\text{Ag}(\text{s}) + \text{O}_2(\text{g}) + 2\text{H}_2\text{O} \rightarrow 4\text{Ag}^+ + 4\text{OH}^-$; $E < 0$, non spontaneous

30. Calculate the potential generated by a cell consisting of a half-cell of 0.5M iron sulphate (III) and 0.1M iron sulphate (II) and another half-cell consisting of an acidic solution at pH=3.5 of potassium permanganate 10^{-2} M and $\text{Mn}^{2+} 10^{-4} \text{ M}$ at 1 atm pressure and temperature of 40 °C.

Data: $E^0(\text{MnO}_4^-/\text{Mn}^{2+}) = 1.51 \text{ V}$; $E^0(\text{Fe}^{3+}/\text{Fe}^{2+}) = 0.77 \text{ V}$; $R = 8.314 \text{ J/mol}\cdot\text{K}$; $F = 96500 \text{ C}$

Solution: $E = 0.392 \text{ V}$

31. Calculate the concentration of Ag^+ ion in moles per liter in the following cell



where $E = 0.36 \text{ V}$.

Data: $E^0(\text{Cu}^{2+}/\text{Cu}) = 0.34 \text{ V}$; $E^0(\text{Ag}^+/\text{Ag}) = 0.80 \text{ V}$.

Solution: $[\text{Ag}^+] = 6.38 \cdot 10^{-3} \text{ M}$

32. For a cell $\text{Zn}|\text{Zn}^{2+}||\text{Cd}^{2+}|\text{Cd}$ at 25 °C of temperature. Find the following: (a) The normal cell potential and electromotive force given that $[\text{Zn}^{2+}] = 0.015$ and $[\text{Cd}^{2+}] = 0.02\text{M}$; (b) The equilibrium constant of the reaction that takes place.

Data: $E^0(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V}$; $E^0(\text{Cd}^{2+}/\text{Cd}) = -0.403 \text{ V}$.

Solution: (a) $E^0 = 0.357$ and $E = 0.361 \text{ V}$; (b) $1.26 \cdot 10^{12}$.

33. A galvanic cell is built according to the following procedure: one electrode consists of a platinum wire introduced in a beaker containing $\text{Fe}^{2+} 1\text{M}$ and $\text{Fe}^{3+} 1\text{M}$; the other half-cell consists of a solid indium block submerged in a solution containing $\text{In}^{3+} 1\text{M}$. Answer the following questions: (a) Which is the electrode with negative polarity? (b) In which electrode takes place the reduction reaction? (c) Write the balanced spontaneous reaction. Which is the normal cell potential? (d) Calculate the equilibrium constant for the redox reaction; (e) If In^{3+} concentration is reduced, how will be modified the cell potential?

Data: $E^0(\text{In}^{3+}/\text{In}) = -0.34 \text{ V}$; $E^0(\text{Fe}^{3+}/\text{Fe}^{2+}) = 0.77$

Solution: (a) In/In^{3+} ; (b) Cathode; (c) $3\text{Fe}^{3+} + \text{In}^0 \rightarrow \text{In}^{3+} + 3\text{Fe}^{2+}$; $E = 1.11 \text{ V}$; (d) $2.76 \cdot 10^{56}$; (e) Potential will increase