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May 2025

Faculty of Natural and Life Sciences
Module: Thermodynamics and Chemistry of Mineral solutions

Name: ..... Surname: ..... Group:

Exam

Exercise 1

Consider the following cell: **Cu / Cu^{2+} (0.5M) // Fe^{3+} (0.2M), Fe^{2+} (0.1M) / Pt**

Data: E° (Fe^{3+}/Fe^{2+}) =0.77V; E°(Cu^{2+}/Cu)=0.34V

1- Write the ox-red half-equations and the overall reaction كتابة معادلتي الاكسدة والارجاع والمعادلة الكلية.

(−) Anode: oxidation: $Cu \longrightarrow Cu^{2+} + 2\bar{e}$ ...0,5...

(+) Cathode: Reduction: $(Fe^{3+} + 1\bar{e} \longrightarrow Fe^{2+}) \times 2$ ...0,5...

Overall reaction: $Cu + 2Fe^{3+} \longrightarrow Cu^{2+} + 2Fe^{2+}$ ...0,5...

2- Calculate the anode and cathode potentials.

$E^{\oplus} = E^{\circ}(Fe^{3+}/Fe^{2+}) + \frac{0,06}{1}\log\frac{(Fe^{3+})}{(Fe^{2+})} = 0,77 + 0,06\log\frac{0,2}{0,1}$ ...0,2... ...0,5...

$E^{\ominus} = E^{\circ}_{Cu^{2+}/Cu} + \frac{0,06}{2}\log(Cu^{2+}) = 0,34 + \frac{0,06}{2}\log 0,5$ ...0,2... | $E^{+} = 0,788V$ ...0,5...

$E^{\ominus} = 0,33V$ ...0,2...

3- Calculate the electromotive force (EMF)) of the cell. ...0,2...

$E_{cell} = E^{\oplus} - E^{\ominus} = 0,788 - 0,33 = 0,458V$ ...0,2...

4- Calculate the equilibrium constant. احسب ثابت التوازن.

$K = 10^{\frac{n\Delta E^{\circ}}{0,06}} = 10^{\frac{2\times(0,77-0,34)}{0,06}} = 10^{14,33}$ ...0,5... ...0,2... ...0,2...

$= 2,13\times10^{14}$ ...0,5...

Exercise 2

The kinetics of the second-order reaction below is studied in aqueous solution at 343 K.

$$ClO^-_{(aq)} \rightarrow 1/3\ ClO_3^-{}_{(aq)} + 2/3\ Cl^-_{(aq)}$$

Data: $[ClO^-]_0$ =0.1M; K =3,1 .10^{-3} $mol^{-1}.L.s^{-1}$.

1- Give the expression of the rate law for the reaction. اعطاء عبارة سرعة التفاعل

$v = +\frac{3}{3}\frac{d[ClO^-]}{dt} = +\frac{3}{2}\frac{d[Cl^-]}{dt} = -\frac{d(ClO^-)}{dt} = k.[ClO^-]^2$ ...1...

2- Calculate the half-life ($T_{1/2}$) of the reaction. حساب زمن نصف التفاعل

$\frac{1}{(ClO^-)_t} - \frac{1}{(ClO^-)_0} = k.t$ / $t = T_{\frac{1}{2}} \Rightarrow (ClO^-) = \frac{(ClO^-)_0}{2}$

$T_{\frac{1}{2}} = \frac{1}{k}\left(\frac{1}{(ClO^-)_0}\right) = \frac{1}{3,1\times10^{-3}}\times\frac{1}{0,1} = 3225,8s$ ...0,5... ...0,5...

3- Calculate the time t_1 required to consume 30% of the initial quantity of ClO^- . الزمن الازم لتفاعل نسبة من الكمية الابتدائية

30% of $(ClO^-)_0$ consumed, Then 70% remains

$[ClO^-]_0 = 0,1\ M$; $(ClO^-)_t = \frac{70}{100} \times 0,1 = 0,07\ M$ (0,25)

(0,25) $\frac{1}{(ClO^-)_t} - \frac{1}{(ClO^-)_0} = k t_1 \Rightarrow t_1 = \frac{1}{k}\left(\frac{1}{(ClO^-)_t} - \frac{1}{(ClO^-)_0}\right)$

$t_1 = \frac{1}{3,1 \times 10^{-3}}\left(\frac{1}{0,07} - \frac{1}{0,1}\right) = 1382,48\ s$ (0,25) (0,25)

Exercise 3

I- To 1L of an aqueous solution of the acid HF with concentration C_{HF} = 0, 2 M, 4.2g of solid NaF is added without any change in volume. (تضيف الملح الى الحمض دون تغير الحجم)

Data: pK_a (HF/F⁻) = 3,18 ; M_{NaF} = 42 g.mol^{-1}

1- What is the nature of the solution obtained? Justify. (ماهو نوع المحلول الناتج مع التعليل) (0,25)

The nature of solution is a buffer solution because it consists a weak acid (HF) and its conjugate base (F^-) (0,5)

2- Calculate the pH value of this solution. (0,25)

(0,25) $pH = pK_a + \log\frac{(F^-)}{(HF)} = 3,18 + \log\frac{4,2/42}{0,2} = 2,87$ (0,25)

II- Fluoride ions and barium ions form the salt BaF_2. pK_{sp} (BaF_2) = 5,86

1- Calculate solubility S of BaF_2 in water . (احسب ذوبانية الملح في الماء)

(0,25) $BaF_2 \rightleftharpoons Ba^{2+} + 2F^-$ | $K_{sp} = 4S^3 \Rightarrow S = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$ (0,25)

$\epsilon = 0$: 0 0 (0,25)

$\epsilon \neq$: S $2S$ (0,25)

(0,25) $K_{sp} = [Ba^{2+}][F^-]^2$ | $S = \left(\frac{10^{-5,86}}{4}\right)^{\frac{1}{3}} = 1 \times 10^{-3}\ M$ (0,25) (0,25)

Exercise 4

Isochoric

A Isobaric B Isothermal C

A	B	C
$P_A = 1,75$ atm	$P_B = P_A$	$P_C = ?$
$V_A = 48,8$ L	$V_B = 2V_A$	$V_C = V_A$
$T_A = 347,15$ K	$T_B = 694,3$ K	$T_C = T_B$

(0,25)

1- Calculate: P_C.

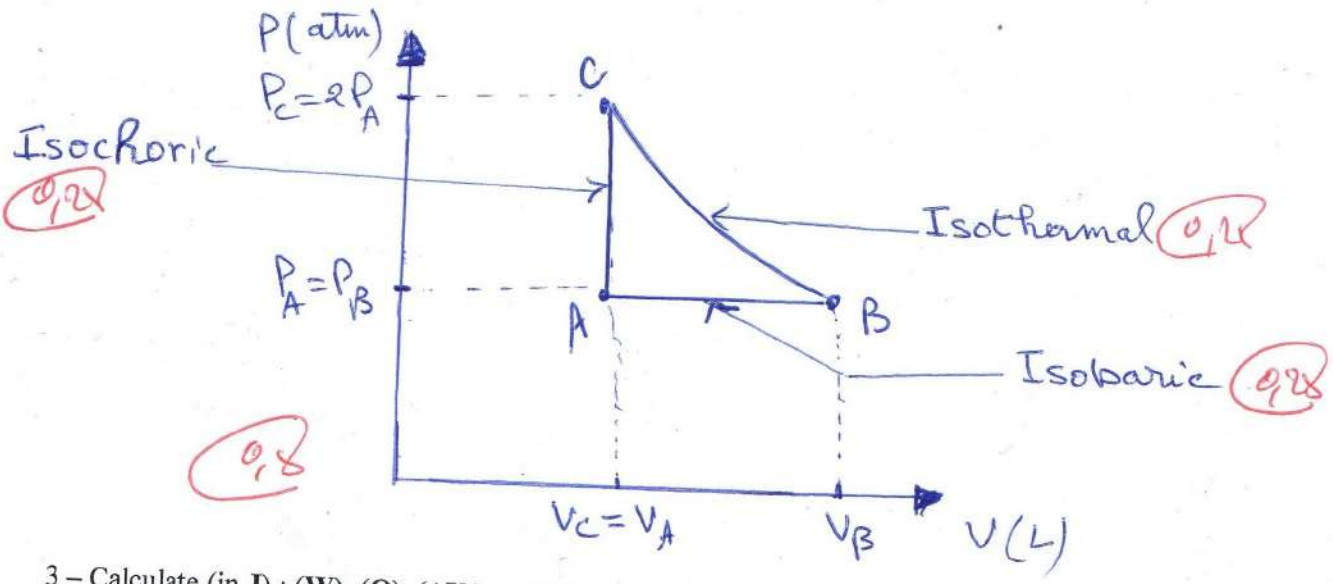
$T_B = T_C = T$

$P_B \cdot V_B = nRT$ } $\Rightarrow P_B V_B = P_C \cdot V_C$
$P_C \cdot V_C = nRT$ }

$P_A = P_B$
$V_B = 2V_A$ } $\Rightarrow P_A \times (2V_A) = P_C \cdot V_A \Rightarrow P_C = 2P_A$
$V_C = V_A$

(0,5) $\Rightarrow P_C = 2 \times 1,75$ atm
$= 3,5$ atm
$= 3,5 \times 1,013 \times 10^5$
$P_C = 3,545 \times 10^5$ Pa

2- Represent the PV diagram.



3 – Calculate (in **J**),: **(W)**, **(Q)**, **(ΔU)** , **(ΔH)** and **(ΔS).**

	W	Q	ΔU	ΔH	ΔS
A-B	$W_{AB} = -P_A(V_B - V_A)$ (0,25) $= 1,75 \times 1,013 \times 10^5 \times (97,6 - 48,8) \times 10^{-3}$ (0,25) $= -8651,02$ J	$Q_P = nC_p(T_B - T_A)$ (0,25) $= 21807,96$ J	$\Delta U = Q + W$ (0,25) $= 21807,96 - 8651,02$ $= 13156,94$ J	$\Delta H = nC_p(T_B - T_A)$ (0,25) $= 3 \times 20,94 \times (694,3 - 347,15)$ $= 21807,96$ J	$\Delta S = nC_p \ln \frac{V_B}{V_A}$ (0,25) $= nC_p \ln \frac{2V_A}{V_A}$ $= 3 \times 20,94 \times \ln 2$ $= 43,54$ J K^{-1} (0,25)
B-C	$W_{B-C} = -nRT \ln \frac{V_C}{V_B}$ (0,25) $= -nRT \ln \frac{V_A}{2V_A}$ (0,25) $= -3 \times 8,314 \times 694,3 \ln \frac{1}{2}$ $= 12003,385$ J	$Q = -W$ (0,25) $= -12003,385$ J (0,25)	$\Delta U = 0$ (0,25)	$\Delta H = 0$ (0,25)	$\Delta S = nR \ln \frac{V_C}{V_B}$ (0,25) $= nR \ln \frac{V_A}{2V_A}$ $= 3 \times 8,314 \times \ln 0,5$ $= -17,29$ J K^{-1} (0,25)
C-A	$W = 0$ (0,25)	$Q = \Delta U$ $= -13143,09$ J (0,25)	$\Delta U = nC_v(T_A - T_C)$ (0,25) $= 3 \times 12,62 \times (347,15 - 694,3)$ $= 13143,09$ J	$\Delta H = nC_p(T_A - T_C)$ (0,25) $= 3 \times 20,94 \times (347,15 - 694,3)$ $= -21807,96$ J (0,25)	$\Delta S = nC_v \ln \frac{T_A}{T_C}$ (0,25) $= 3 \times 12,62 \ln \frac{347,15}{694,3}$ $= -26,24$ J K^{-1} (0,25)