

P3
80

Solution 1

(a)

i)

$$\left(\frac{dG}{d\xi}\right)_{T,P} = \Delta G_{rxn}^{\circ} + RT \ln \prod_{i=1}^N a_{i,eq}^{\nu_i} \quad (1 \text{ mk})$$

$$\prod_{i=1}^N a_{i,eq}^{\nu_i} = \frac{a_C}{a_A a_B} = \frac{P_C}{P_A P_B} = \frac{0.25 \text{ bar}}{(1 \text{ bar})(0.5 \text{ bar})} = 0.5 \text{ bar} \quad (1 \text{ mk})$$

For an ideal gas $a_i = P_i$

$$\begin{aligned} \left(\frac{dG}{d\xi}\right)_{T,P} &= -10000 \frac{\text{J}}{\text{mol}} + \left(8.3145 \frac{\text{J}}{\text{K mol}}\right) (298.15 \text{ K}) \ln(0.5 \text{ bar}) \\ &= -11.718 \frac{\text{kJ}}{\text{mol}} \end{aligned} \quad (2 \text{ mks})$$

ii)

$$\Delta G^{\circ} = -RT \ln K_{eq} \quad (1 \text{ mk})$$

$$\ln K_{eq} = -\frac{\Delta G^{\circ}}{RT}$$

$$\ln K_{eq} = -\frac{\left(-10000 \frac{\text{J}}{\text{mol}}\right)}{\left(8.3145 \frac{\text{J}}{\text{mol K}}\right) (298.15 \text{ K})} = 4.0339 \quad (1 \text{ mk})$$

$$K_{eq} = e^{4.0339} = 56.483 \quad (0.5 \text{ mk})$$

$$Q = \prod_{i=1}^N a_{i,eq}^{\nu_i} < K_{eq} \text{ (reaction moves forward)}$$

iii)

	$A(g) + B(g) \rightleftharpoons C(g)$	
Initial press	1 0.5 0.25	
Change	- ξ - ξ + ξ	
Press at equilibrium	1 - ξ 0.5 - ξ 0.25 + ξ	(2 mks)
Total press	1 - ξ + 0.5 - ξ + 0.25 + ξ = 1.75 - ξ	

$$K_{eq} = \frac{P_C}{P_A P_B} = \frac{(0.25 + \xi)}{(1 - \xi)(0.5 - \xi)} = 56.483 \quad (1.5 \text{ mks})$$

(1 mk)

$$56.483x^2 - 85.7245x + 27.9915 = 0$$

$$a=56.483, b=-85.7245, c=27.9915$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-(-857245) \pm \sqrt{(-857245)^2 - 4(56.483)(27.9915)}}{2(56.483)} \quad (1 \text{ mk})$$

$$x = \frac{857245 \pm \sqrt{1024.514322}}{112.966}$$

$$x = 1.0422 \text{ or } x = 0.476$$

(1 mk)

$$P_A = 1 - 0.476 = 0.5244$$

(0.5 mk)

$$P_B = 0.5 - 0.476 = 0.0244$$

(0.5 mk)

$$P_C = 0.25 - 0.476 = 0.726$$

(0.5 mk)

(b)

$$P = \frac{n}{V} RT \quad (1 \text{ mk})$$

$$0.496 \text{ bar} = (1 + \xi) \left(5.96 \times 10^{-3} \frac{\text{mol}}{\text{L}} \right) \left(0.08314 \frac{\text{L} \cdot \text{bar}}{\text{K} \cdot \text{mol}} \right) (973 \text{ K}) \quad (1 \text{ mk})$$

$$\xi = \frac{0.496 \text{ bar}}{\left(5.96 \times 10^{-3} \frac{\text{mol}}{\text{L}} \right) \left(0.08314 \frac{\text{L} \cdot \text{bar}}{\text{K} \cdot \text{mol}} \right) (973 \text{ K})} - 1 \quad (1 \text{ mk})$$

$$\xi = 0.0288 \quad (1 \text{ mk})$$

$$K = \frac{4\xi^2 \left(\frac{P}{p^\circ} \right)}{(1 - \xi^2)} = \frac{4(0.0288)^2 (0.496)}{(1 - 0.0288^2)} = 1.64 \times 10^{-3} \quad (1.5 \text{ mks})$$

Solution 2

(a) $T_1 = 25.0^\circ\text{C} = 298 \text{ K}$

1 mark

$$T_2 = -60^\circ\text{C} = 213 \text{ K}$$

1 mark

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

2 marks

$$\ln \frac{1.08 \times 10^7}{6.02 \times 10^7} = -\frac{E_a}{8.3145} \left(\frac{1}{213} - \frac{1}{298} \right)$$

4 marks

$$-1.718 = -(-1.6106) E_a$$

$$= 10666.85 \text{ J/mol}$$

4 marks

$$= 10.7 \text{ kJ/mol}$$

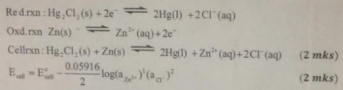
$\frac{0.00418}{2} = 2.09 \times 10^{-3}$
 $\frac{0.0295}{2}$

- (ii) NO 1 mark
- (iii) $O_3 + NO \rightarrow NO_2 + O_2$ 1 mark
- (iv) O_3 once and O is not used 1 mark
- (v) $R = k[O_3]$ 1 mark

ion 4

- a) $\log \gamma_{\pm} = -0.509 L mol^{-1})^{1/2} [z_+ z_-]^{1/2}$ (2 mks)
 $l = 3c$
 $\log \gamma_{\pm} = -0.509 L mol^{-1})^{1/2} [2 \times -1 \cdot (3 \times 0.00500 mol L^{-1})^{1/2}]$ (2 mks)
 $\log \gamma_{\pm} = -0.12468$
 $\gamma_{\pm} = 10^{-0.12468} = 0.75045$ (2 mks)

b)



c)

$a_{ZnCl_2} = (m_{\gamma_{\pm}})^1 (2m_{\gamma_{\pm}})^2 = 4m^3 \gamma_{\pm}^3$ (2 mks)
 $E_{cell} = E_{cell}^{\circ} - \frac{0.05916}{2} \log 4m^3 \gamma_{\pm}^3$ (2 mks)
 $E_{cell}^{\circ} = [0.2676 - (-0.7628)] V = 1.0304 V$ (1 mks)
 $E_{cell} = 1.0304 - \frac{0.05916}{2} \log 4(0.00500)^3 (0.75045)^3$ (2 mks)
 $E_{cell} = 1.0304 V + 0.19745 V$ (2 mks)
 $E_{cell} = 1.2278 V$ (2 mks)

$$56.483x^2 - 85.7245x + 27.9915 = 0$$

(1 mk)

$$a=56.483, b=-85.7245, c=27.9915.$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-(-85.7245) \pm \sqrt{(-85.7245)^2 - 4(56.483)(27.9915)}}{2(56.483)}$$

(1 mk)

$$x = \frac{85.7245 \pm \sqrt{1024.514322}}{112.966}$$

$$x = 1.0422 \text{ or } x = 0.476$$

(1 mk)

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(0.5 mk)

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(1 mk)

$$0.496 \text{ bar} = (1 + \xi) \left(5.96 \times 10^{-3} \frac{\text{mol}}{\text{L}} \right) \left(0.08314 \frac{\text{L} \cdot \text{bar}}{\text{K} \cdot \text{mol}} \right) (973 \text{ K})$$

(1 mk)

$$\xi = \frac{0.496 \text{ bar}}{\left(5.96 \times 10^{-3} \frac{\text{mol}}{\text{L}} \right) \left(0.08314 \frac{\text{L} \cdot \text{bar}}{\text{K} \cdot \text{mol}} \right) (973 \text{ K})} - 1$$

(1 mk)

$$\xi = 0.0288$$

(1 mk)

$$K = \frac{4\xi^2 \left(\frac{P}{p^\circ} \right)}{(1 - \xi^2)} = \frac{4(0.0288)^2(0.496)}{(1 - 0.0287^2)} = 1.64 \times 10^{-3}$$

(1.5 mks)

Solution 2

(a) $T_1 = 25.0^\circ\text{C} = 298 \text{ K}$

1 mark

$$T_2 = -60^\circ\text{C} = 213 \text{ K}$$

1 mark

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

2 marks

$$\ln \frac{1.08 \times 10^7}{6.02 \times 10^7} = -\frac{E_a}{8.3145} \left(\frac{1}{213} - \frac{1}{298} \right)$$

4 marks

$$-1.718 = -(-1.6106) E_a$$

$$= 10666.85 \text{ J/mol}$$

4 marks

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(b) $\ln [A]_t = \ln [A]_0 + \lambda_d t_d$ 2 marks

$\lambda_d = \frac{\ln 2}{t_d} = \frac{0.693}{50} = 0.01386$ 2 marks

$\ln [A]_t = \ln 1 + 0.01386 \times 70$ 2 marks

$\ln \frac{[A]_t}{[A]_0} = 0.9702$

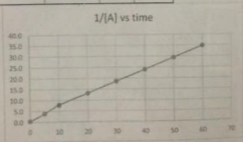
$\frac{[A]_t}{[A]_0} = 2.64$ 2 marks

Solution 3

(a) Table 4 marks

Time (minutes)	[NO ₂] (M)	ln[A]	1/[A]
0	2.4	0.88	0.4
5	2.60E-01	-1.35	3.8
10	1.28E-01	-2.06	7.8
20	7.58E-02	-2.58	13.2
30	5.38E-02	-2.92	18.6
40	4.17E-02	-3.18	24.0
50	3.40E-02	-3.38	29.4
60	2.87E-02	-3.55	34.8

$r = k[A]^2$



Graph: Axis label, Units an title 2 marks
 Chosen correctly and Data plotted correctly 3 marks

Straight line graph is second order. Hence, the order of reaction is 2. 2 marks

Slope = $k = 0.56449502$ 2 marks
 Units = $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ 2 marks

1 mark

(b) (i) NO₂