Chemical Equilibrium Marking Scheme

2017 Q7

QUESTION 7

(*a*) WHAT: state in which **rate of forward reaction** is **equal to rate of reverse reaction /** state reached at which **concentrations of reactants and products** are **constant** **(5)**
[Allow $r_f = r_r$ or $r_f = r_b$.]

WHY: both **reaction(s) continue(s) / reaction doesn't stop** (3)

STATE: systems **in (at) equilibrium //**
react to **oppose (minimise, relieve)** applied **stress(es) {disturbance(s)}** (2 × 3)
[Instead of '*stress(es){disturbance(s)}*' accept '*change in temperature, pressure or number of moles (concentrations)*' if all three {temperature, pressure and moles (concentrations)} are given.]

(*b*) WRITE: $K_c = \dfrac{[NO_2]^2}{[N_2O_4]}$ (6)
[Do not accept inverted expression.]

(*c*) CALCULATE: **0.05** mol per litre $\mathbf{N_2O_4}$ and **0.1** mol per litre $\mathbf{NO_2}$ (18)

Candidate takes 2*x* moles/l NO_2 at equilibrium

$N_2O_{4\,(g)} \leftrightharpoons 2NO_{2\,(g)}$

Start: 1 mol — 0 mol
0.1 mol/l — 0 mol/l (3)

Equil: **0.1 – *x*** mol/l — **2*x*** mol/l (3)

$\dfrac{4x^2}{0.1-x} = 0.2$ / $\dfrac{(2x)^2}{0.1-x} = 0.2$ /

$4x^2 + 0.2x - 0.02 = 0$ / $2x^2 + 0.1x - 0.01 = 0$ /

$x^2 + 0.05x - 0.005 = 0$ (3)

$x = \dfrac{-(0.2)\pm\sqrt{(0.2)^2-4(4)(-0.02)}}{2\times4}$ /

$x = \dfrac{-(0.1)\pm\sqrt{(0.1)^2-2(-0.01)}}{2\times2}$ /

$x = \dfrac{-(0.05)\pm\sqrt{(0.05)^2-4(-0.005)}}{2}$

or $(2x + 0.2)(2x – 0.1) = 0$ / $(x + 0.1)(2x – 0.1) = 0$ / $(x + 0.1)(x – 0.05) = 0$

x = **0.05** mol/l (3)

$[N_2O_4]$ = $0.1 – x$ = **0.05** mol/l (3)
$[NO_2]$ = $2x$ = **0.1** mol/l (3)

Candidate takes *y* moles/l NO_2 at equilibrium

$N_2O_{4\,(g)} \leftrightharpoons 2NO_{2\,(g)}$

Start: 1 mol — 0 mol
0.1 mol/l — 0 mol/l (3)

Equil: **0.1 – ½*y*** mol/l — ***y*** mol/l (3)

$\dfrac{y^2}{0.1-½y} = 0.2$ /

$y^2 + 0.1y - 0.02 = 0$ (3)

$y = \dfrac{-(0.1)\pm\sqrt{(0.1)^2-4(-0.02)}}{2}$

or $(y + 0.2)(y – 0.1) = 0$

y = **0.1** mol/l (3)

$[N_2O_4]$ = $0.1 – ½y$ = **0.05** mol/l (3)
$[NO_2]$ = y = **0.1** mol/l (3)

Candidate working with $2x$ moles $\mathbf{NO_2}$ at equilibrium

	$\mathbf{N_2O_4}$ *(g)*	$\leftrightharpoons$	$\mathbf{2NO_2}$ *(g)*	
Start:	1 mol		0 mol	
Equil:	$\mathbf{1 - x}$ mol		$\mathbf{2x}$ mol	(3)
Equil:	$\mathbf{(1 - x) \div 10}$ mol/l		$\mathbf{2x \div 10}$ mol/l	(3)

$\frac{4x^2 \div 100}{(1-x) \div 10}$ **= 0.2** / $\frac{(\frac{2x}{10})^2}{(\frac{1-x}{10})}$ **= 0.2** / $\frac{4x^2}{(1-x)}$ **= 2** /

$\mathbf{4x^2 + 2x - 2 = 0}$ **/**

$\mathbf{2x^2 + x - 1 = 0}$ **/** $\mathbf{x^2 + 0.5x - 0.5 = 0}$ (3)

$x = \frac{-(2) \pm \sqrt{(2)^2 - 4(4)(-2)}}{2 \times 4}$ /

$x = \frac{-(1) \pm \sqrt{(1)^2 - 4(2)(-1)}}{2 \times 2}$ /

$x = \frac{-(0.5) \pm \sqrt{(0.5)^2 - 4(-0.5)}}{2}$

or $(2x + 2)(2x - 1) = 0$ / $(2x - 1)(x + 1) = 0$ / $(x + 1)(x - 0.5) = 0$

x = **0.5** mol (3)

$\mathbf{[N_2O_4]}$ = $(1 - x) \div 10 =$ **0.05** mol/l (3)
$\mathbf{[NO_2]}$ = $2x \div 10 =$ **0.1** mol/l (3)

Candidate working with y moles $\mathbf{NO_2}$ at equilibrium

	$\mathbf{N_2O_4}$ *(g)*	$\leftrightharpoons$	$\mathbf{2NO_2}$ *(g)*	
Start:	1 mol		0 mol	
Equil:	$\mathbf{1 - ½y}$ mol		$\mathbf{y}$ mol	(3)
Equil:	$\mathbf{(1 - ½y) \div 10}$ mol/l		$\mathbf{y \div 10}$ mol/l	(3)

$\frac{y^2 \div 100}{(1-½y) \div 10}$ **= 0.2** / $\frac{y^2}{1-½y}$ **= 2** /

$\mathbf{y^2 + y - 2 = 0}$ (3)

$y = \frac{-(1) \pm \sqrt{1^2 - 4(-2)}}{2}$

or $(y + 2)(y - 1) = 0$

y = **1** mol (3)

$\mathbf{[N_2O_4]}$ = $(1 - ½y) \div 10 =$ **0.05** mol/l (3)
$\mathbf{[NO_2]}$ = $y \div 10 =$ **0.1** mol/l (3)

[Chemically impossible solution of correct quadratic equation also used to find concentrations, deduct (1) mark.]
[Do not award last (6) marks for quadratic equation with two chemically impossible solutions.]
[Do not allow mixing and matching of marks within boxes.]
[Where inverted K_c expression used, do not award (3) marks for setting up quadratic.]

(d) EXPLAIN: **low(er) temperature (decrease in temperature) favours (results in, produces more)** $\mathbf{N_2O_4}$ **{left side, reverse, exothermic (heat producing)** reaction**} /**

high(er) temperature would **favour (result in, produce more)** $\mathbf{NO_2}$ **{right side, forward, endothermic (heat absorbing)** reaction**}** (3)

DEDUCE: decomposition **endothermic** (3)
[Linkage here. EXPLAIN marks only available if DEDUCE marks awarded but order of answering parts unimportant]

(e) WOULD: **no** change (effect) **/ none** (3)

EXPLAIN: $\mathbf{K_c}$ **constant at given temperature** even if concentrations change **/ only change in temperature will result in change in** $\mathbf{K_c}$ (3)
[WOULD and EXPLAIN linked; order of answering parts unimportant; WOULD marks may be awarded if correct response to WOULD is inferred in correct EXPLAIN statement.]

2016 Q7

QUESTION 7

(*a*) STATE: systems **in (at) equilibrium** //
react to **oppose (minimise, relieve)** applied **stress(es) {disturbance(s)}** **(3 + 2)**
[Instead of 'stress(es){disturbances}' accept 'change in temperature, pressure or number of moles (concentrations)' if all three {temperature, pressure and moles (concentrations)} are given.]

PREDICT: (*i*) **low** temperature //
[Allow 'decrease in temperature'.]

EXPLAIN: **favours (results in, produces more) exothermic (heat producing)** reaction / **high temperature** would **favour (result in, produce more) endothermic (heat absorbing)** reaction / favours **forward reaction** which **is exothermic / does not favour reverse reaction which is endothermic** (2 × 3)

PREDICT: (*ii*) **high** pressure //
[Allow 'increase in pressure'.]

EXPLAIN: **favours (results in, produces) fewer moles (molecules) / favours smaller volume / low pressure** would **favour (result in, produce) more moles (molecules) / favours greater volume** / favours **fewer moles (molecules) on right** / favours **smaller volume on right / does not favour more moles (molecules) on left / does not favour greater volume on left /**
(2 × 3)
[EXPLAIN marks only available if PREDICT marks awarded.]

EXPLAIN: reaction (rate) too **slow (uneconomical, costly)** at low temperatures (3)

(*b*) STATE: **no effect / none** (3)

EXPLAIN: in presence of catalyst **sulfur trioxide (SO_3) produced and used up at same rate** / catalyst **alters (speeds up) rate of forward and reverse** reactions **equally** (3)
[EXPLAIN marks linked to STATE marks.]['*Equilibrium reached faster*' insufficient on its own.]

(*c*) WRITE: $K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$ (6)

CALCULATE: **196000 / 1.96 × 10⁵** (18)

Initially: moles $SO_2 = \frac{96}{64^*}$ = **3/2 (1.5)** and moles $O_2 = \frac{24}{32^*}$ = **3/4 (0.75)** (3)

At equilibrium: moles $SO_3 = \frac{112}{80^*}$ = **7/5 (1.4)** (3)

	$2SO_2$ +	O_2 ⇋	$2SO_3$
Equil mol:	**0.1** (3)	**0.05** (3)	1.4
Equil M:	**0.002**	**0.001**	**0.028**
			Divide by 50. (3)

	$2SO_2$ +	O_2 ⇋	$2SO_3$
Initial M:	**0.03**	**0.015**	
Equil M:			**0.028**
			Divide by 50. (3)
Equil M:	**0.002** (3)	**0.001** (3)	0.028

$K_c = \frac{(0.028)^2}{(0.002)^2(0.001)}$ = **196000 / 1.96 × 10⁵** (3)

[**Addition must be shown for error to be treated as slip.*]

[*Where **K**$_c$ incorrect, e.g. inverted, allow consequential marks for calculation – up to a maximum of 15 marks.*]

$2SO_2 + O_2 \leftrightharpoons 2SO_3$

Start (moles):	$\frac{96}{64^*}$ = **3/2(1.5)**	$\frac{24}{32^{**}}$ = **3/4 (0.75)**		(3)
Equil (moles):			$\frac{112}{80^{***}}$ = **7/5 (1.4)**	(3)
Equil (moles):	$(1.5 - 2x)$	$(0.75 - x)$	$2x = 1.4$	$x = 0.7$
Equil (moles):	**0.1**	**0.05**	1.4	(2 × 3)
Equil (mol/L):	0.1 ÷ 50 = **0.002**	0.05 ÷ 50 = **0.001**	1.4 ÷ 50 = **0.028**	Divide by 50. (3)

$K_c = \frac{(0.028)^2}{(0.002)^2(0.001)}$ = **196000 / 1.96 × 10⁵** (3)

$2SO_2 + O_2 \leftrightharpoons 2SO_3$

Start (moles):	$\frac{96}{64^*} = \frac{3}{2}$ / **1.5**	$\frac{24}{32^{**}} = \frac{3}{4}$ / **0.75**		(3)
Equil (moles):			$\frac{112}{80^{***}} = \frac{7}{5}$ / = **1.4**	(3)
Start (mol/L):	1.5 ÷ 50 = **0.03**	0.75 ÷ 50 = **0.015**	0 1.4 ÷ 50 = 0.028	Divide by 50. (3)
Equil (mol/L):	$(0.03 - 2x)$	$(0.015 - x)$	$2x$ = 0.028	x = 0.014
Equil (mol/L):	**0.002**	**0.001**	0.028	(2 × 3)

$K_c = \frac{(0.028)^2}{(0.002)^2(0.001)}$ = **196000 / 1.96 × 10⁵** (3)

2015 Q11 b)

(*b*) CALC: **50** mol (13)

A ⇋ B + C Start: 3.0 mol / L, 0 mol / L, 0 mol / L Equil: **(3 – x)** (3), x, x (3) $K_c = \frac{(x)^2}{(3.0-x)} = 4$ (3) $x^2 + 4x - 12.0 = 0$ $(x+6)(x-2) = 0$ / $x = \frac{-(4)\pm\sqrt{(4)^2-4(1)(-12.0)}}{2}$ x = 2.0 mol / L (3) ⇒ 5.0 mol / L total ⇒ 5.0 × 10 = **50** mol **(1)**	A ⇋ B + C Start: 30 mol, 0 mol, 0 mol Equil: (30 – x), x, x Equil: $(\frac{30-x}{10})$ mol / L(3), $\frac{x}{10}$mol/L, $\frac{x}{10}$mol/L (3) $K_c = \frac{(\frac{x}{10})^2}{(\frac{30-x}{10})} = 4$ / $\frac{(x)^2}{(30-x)} = 40$ (3) $x^2 + 40x - 1200 = 0$ $(x+60)(x-20) = 0$ / $x = \frac{-(40)\pm\sqrt{(40)^2-4(1)(-1200)}}{2}$ x = **20** mol (3) ⇒ **50** mol total **(1)**

[Where no other mark awarded allow (3) for $K_c = \frac{[B][C]}{[A]}$.]

DEDUCE: **endo**thermic (3)

EXPLAIN: ***K*$_c$ increases with temperature / at higher temperature more products (more B and C, more forward reaction, reaction shifts to the right, reaction opposes stress)** (3)

[EXPLAIN marks only available if DEDUCE marks awarded.]

EXPLAIN: **increase //**

more gaseous **product (particles, B and C) / more forward reaction / equilibrium shifts to the right / more collisions** with walls of container / **increased velocity (energy) of** gaseous **molecules (particles) / then (followed by, resulting in)** bringing about of **decrease {reverse, shift backward, shift left, shift to reactant(s), shift to A}** (2 × 3)

[Second (3) only available if first (3) is awarded.]