

Chemistry 225 Semester 04-2016

Homework for Submission #3 –Answer Key

1) a) $K = \frac{[Mn^{2+}][Fe^{3+}]^5}{[Fe^{2+}]^5[MnO_4^-][H^+]^8}$ (1 mark)

b) $K = \frac{(p_{H_2O})^4}{(p_{H_2})^4}$ (1 mark)

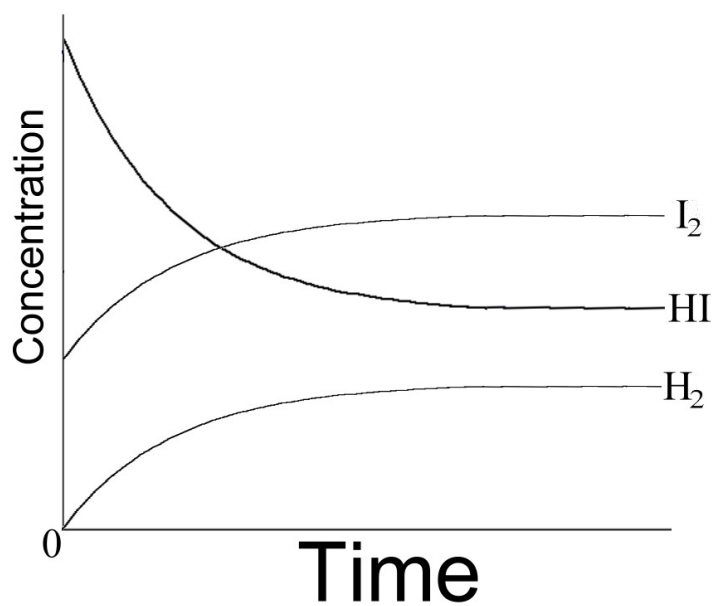
c) $K = \frac{[Fe^{3+}]^2[Cr^{3+}]^2}{[Cr_2O_7^{2-}][H^+]^{14}}$ (1 mark)

d) $K = p_{C_2H_5OH(g)}$ (1 mark)

Note: Unless K_c is specified, gases are always represented by partial pressures in the equilibrium expression.

2) Hydrogen iodide and iodine are introduced into a sealed vessel at a temperature at which both are gases and allowed to react until equilibrium is reached. Sketch:

a) a graph of concentration against time showing the concentrations of hydrogen, iodine and hydrogen iodide.



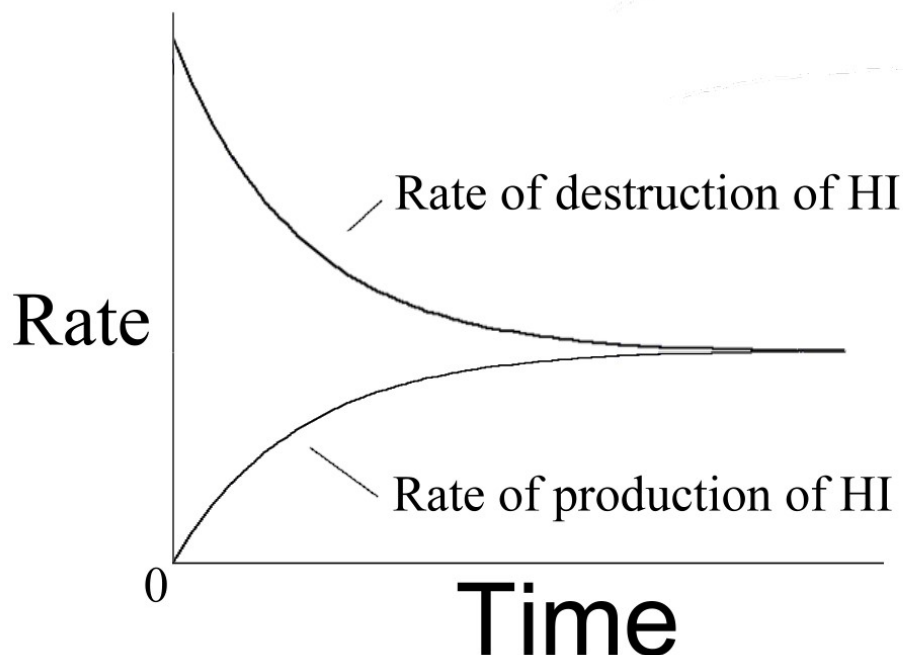
(3 marks)

The reaction is, of course: $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$, which we have met frequently in class. The concentrations of

I_2 and HI are non-zero to begin with, whereas that of H_2 is zero. This latter means that the reverse reaction cannot occur at the beginning, and only the forward reaction occurs, so that the concentration of HI decreases, and the concentrations of H_2 and I_2 increase. Eventually equilibrium is reached and there is no further change in concentrations. Reaction is most rapid at the beginning, meaning that the lines slope steeply. The decrease in concentration of HI is twice the rise in the concentration of I_2 , which is equal to the rise in concentration of H_2 , because of the stoichiometry of the equation (2:1:1).

(The curves were produced mathematically using Excel assuming the reactions are first order, and then copied into a drawing program to produce the final graphs.)

- b) a second graph showing both the rate of production of hydrogen iodide (one curve) and the rate of its reaction (ie. destruction – a second curve) as a function of time.



(3 marks)

There is no H_2 to begin with, so the rate of production of HI must be zero, whilst the rate of its destruction is at its maximum, since its concentration is at its maximum. As HI is turned into H_2 and I_2 the reverse reaction, leading to the production of HI, can get started. Eventually equilibrium is reached at which stage the rates are equal. However, there is no reason to suppose that the rates are equal to half the initial rate of production of HI.

- 3) a) An equilibrium mixture contains 0.0200 mol of bromine, 0.0125 mol of hydrogen and 0.00050 mol of hydrogen bromide at a fixed temperature. Determine the equilibrium constants (K_c) for the reactions represented by
- i) $2HBr(g) \rightleftharpoons H_2(g) + Br_2(g)$ (2 marks)
- ii) $\frac{1}{2}H_2(g) + \frac{1}{2}Br_2(g) \rightleftharpoons HBr(g)$ (2 marks)
- and determine the mathematical relationship between these constants.
Hint: let the volume of the container be $V \text{ dm}^3$.

Solution

Note that equilibrium expressions require concentrations, not numbers of moles. Students must demonstrate that they are aware of this in order to obtain a good mark. Note also that whilst the volume of the container cancels in this case, it is not usually so.

$$K_{Ci} = \frac{[H_2][Br_2]}{[HBr]^2} = \frac{\left(\frac{0.0125}{V}\right)\left(\frac{0.0200}{V}\right)}{\left(\frac{0.0005}{V}\right)^2} = \frac{0.0125 \times 0.02}{0.0005^2} = \frac{2.5 \times 10^{-4}}{2.5 \times 10^{-7}} = \underline{\underline{10000}}$$

$$K_{Cii} = \frac{[HBr]}{[H_2]^{1/2}[Br_2]^{1/2}} = \frac{\left(\frac{0.0005}{V}\right)}{\left(\frac{0.0125}{V}\right)^{1/2}\left(\frac{0.02}{V}\right)^{1/2}} = \frac{0.0005}{\sqrt{0.0125} \times \sqrt{0.02}} = \frac{5 \times 10^{-4}}{\sqrt{2.5 \times 10^{-4}}} = \frac{\sqrt{25} \times 10^{-4}}{\sqrt{2.5} \times 10^{-2}} = \sqrt{\frac{25}{2.5}} \times 10^{-2}$$

= $10^{-2} \sqrt{10}$ or 0.032 to 2 s.f.)

The mathematical relationship between the equilibrium constants K_{Ci} and K_{Cii} can be seen from the previous answers:

$$K_{Ci} = \frac{1}{(K_{Cii})^2}$$

(1 mark)

- b) In another experiment conducted *at this same temperature*, some HBr was admitted into an evacuated 2000 cm³ vessel and when equilibrium was attained some had decomposed yielding 6.32 mol of bromine as one product. What was the concentration of each species present at equilibrium? (5 marks)

Solution

The equation is:



whose equilibrium constant is $K_{Ci} = \frac{[H_2][Br_2]}{[HBr]^2} = 1000$ since this is the same reaction at the same temperature as part (a)(i). (Note: the other equation could be used just as well.)

We build up the “ICE” table¹ in terms of moles, representing the initial concentration of HBr by a .

	2HBr(g)	\rightleftharpoons	H ₂ (g)	Br ₂ (g)
Initial /M	a		0	0
Change /M	$-2x$		$+x$	$+x$
Equilibrium /M	$a-2x$		x	x

The volume of the container is 2000 cm³ = 2 dm³. Since the equilibrium number of moles of Br₂ is 6.32, the equilibrium concentration of Br₂, in mol dm⁻³ $x = 6.32/2 = 3.16$ and so

$$K_{Ci} = 1000 = \frac{[H_2]_e[Br_2]_e}{[HBr]_e^2} = \frac{(x)(x)}{(a-2x)^2} = \frac{(3.16)^2}{(a-2x)^2}$$

$$\therefore a - 2x = \sqrt{\frac{(3.16)^2}{1000}} = 0.099927$$

This is the equilibrium concentration of HBr and so, to summarise to 2 significant figures², at equilibrium:

$$\underline{[HBr] = 0.10 \text{ M}, [Br_2] = [H_2] = 3.2 \text{ M}}$$

- 4) A 0.831 g sample of SO₃ is placed in a 1.00 L container and heated to 1100 K. The SO₃ decomposes to SO₂ and O₂ according to the following equation:

¹ We don't really need the ICE table in this case, but it helps to see what is going on.

² 2 significant figures because the equilibrium constant used was determined using a number of moles of hydrogen given to 1 significant figure. Strictly speaking the answer should be presented to 1 significant figure also, but we never normally round to 1 significant figure.



At equilibrium the total pressure in the container is 1.300 atm. Find the value of K_p for this equilibrium at 1100 K. (Hint: develop your table in terms of partial pressures and recall the relationship between total pressure and partial pressures for a mixture.) (4 marks)

$$\# \text{ of moles of SO}_3 = 0.831 \text{ g} \div (32.065 + 3 \times 15.999) \text{ g mol}^{-1} = 0.831 \div 80.062 \text{ mol}$$

$$\text{But } PV = nRT$$

Hence initial pressure of the SO_3 at 1100 K is

$$P = \frac{nRT}{V} = \frac{0.831}{80.062} \times 0.0821 \times 1100 = 0.937369 \text{ atm}$$

	2SO_3	2SO_2	O_2
Initial / atm	0.937369	0	0
Change / atm	-2x	+2x	+x
Equilibrium / atm	$0.937369 - 2x$	2x	x

$$\text{But total equilibrium pressure} = 1.300 \text{ atm} = 0.937369 - 2x + 2x + x = 0.937369 + x$$

$$\therefore x = 1.3 - 0.937369 = 0.362631 \text{ atm}$$

$$\therefore K_p = \frac{(P_{\text{SO}_2})^2 (P_{\text{O}_2})}{(P_{\text{SO}_3})^2} = \frac{(2x)^2 (x)}{(0.937369 - 2x)^2} = \frac{4 \times 0.362631^3}{(0.937369 - 2 \times 0.362631)^2} = 4.23985 = \underline{\underline{4.24 \text{ to 3 sf}}}$$

(Recall that equilibrium constants are unitless.)