KEY – Unit 2 Problem Set A – KEY

1. Water is boiling in a kettle at 100°C. Is the system at equilibrium? Explain.

   solution:

   No. The system is not closed.

2. Ice and water are in a stoppered, insulated flask at 0°C. Is the system at equilibrium? Explain.

   solution:

   Yes. The sytem is closed. The rates of melting and freezing are equal.

3. A chemist wished to prepare pure phosgene, $COCl_2$, by reacting carbon monoxide and chlorine according to the reaction:

   $$CO_{(g)} + Cl_{2(g)} \leftrightarrows COCl_{2(g)}$$

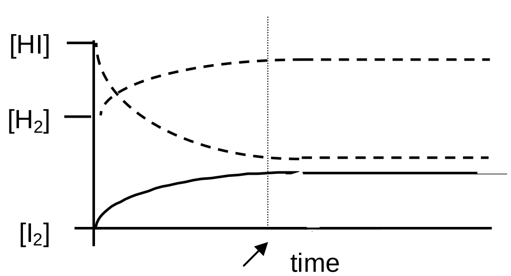
   Why will this reaction not produce pure $COCl_2$? If a pure sample could somehow be obtained would it remain pure?

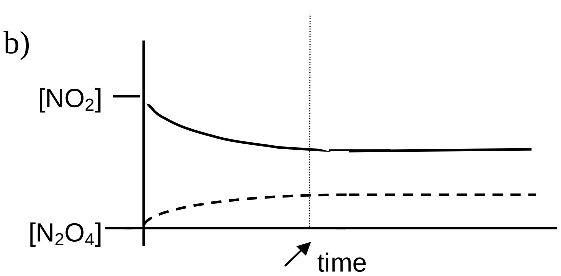
   solution:

   This reaction will not produce pure $COCl_2$ because the phosgene, once made, will immediately begin to undergo the reverse reaction and breaking down to carbon monoxide and chlorine. Even if a pure sample was obtained it cannot remain pure because the reverse reaction would occur spontaneously and start to produce carbon monoxide and chlorine. At equilibrium, reactants and products are all present, and if the system is not at equilibrium, both the forward and reverse reactions will eventually cause an equilibrium to be reached.

4. On the graphs below, sketch the concentration vs. time behaviour of the reactant or product species. Initial concentrations are marked.

   a. $H_2 + I_2 \leftrightarrows 2HI$ b. $2NO_2 \leftrightarrows N_2O_4$

a) 

b) 

solution:

See dashed lines on graphs above.

5. On the graphs above, show where equilibrium is reached.

   solution:

   See dotted vertical lines and arrows on graphs above.

6. Compare the entropy of reactants and products in each of the following:

   a) $I_{2(s)} \leftrightarrows I_{2(g)}$
   b) $HA_{(aq)} \leftrightarrows H^+_{(aq)} + A^-_{(aq)}$

   solution:

   a) *Entropy is greater in the products – gasses have much less order than solids.*

   b) *Entropy is greater in the products – ions in solution have much less order than whole molecules in solution.*

7. For each of the reactions below, predict if the reaction will go to completion, result in an equilibrium, or not happen at all, based on entropy and enthalpy considerations.

   a) $H_2SO_{4(l)} + nH_2O_{(l)} \leftrightarrows H_2SO_{4(aq)} + 150kJ$ (not balanced)
   b) $C_2H_{6(g)} \leftrightarrows C_2H_{2(g)} + 2H_{2(g)}$ $\Delta H = 311kJ$
   c) $I_{2(g)} + Cl_{2(g)} \leftrightarrows 2ICl_{(g)}$ $\Delta H = 35.0kJ$

   solution:

   a) *completion – both entropy and enthalpy favour the products*

   b) *equilibrium – entropy favours the products, enthalpy favours the reactants.*

   c) *no reaction – entropy and enthalpy both favour the reactants. (In reality, this particular reaction <u>might</u> reach an equilibrium which heavily favours the reactants, talk to your teacher if you're interested in knowing why.)*

KEY – Unit 2 Problem Set B – KEY

Use Le Châtelier's principle to describe the shift in equilibrium for the changes in the systems below (questions 1 – 5):

1. $H_{2(g)} + I_{2(g)} \leftrightarrows 2HI_{(g)}$ $\Delta H = +52.7 kJ/mol$
   a) increase $[H_2]$
   b) increase $[HI]$
   c) increase the pressure by lowering the volume
   d) add a catalyst

   solution:

   a) shift right / to products
   b) shift left / to reactants
   c) no shift (equal # gas particles both sides)
   d) no shift (forward & reverse rates increase equally)

2. $2NO_{2(g)} \leftrightarrows N_2O_{4(g)}$
   a) increase $[NO_2]$
   b) decrease $[N_2O_4]$
   c) decrease the pressure by raising the volume
   d) add a catalyst

   solution:

   a) shift right / to products
   b) shift right / to products
   c) shift left / to reactants (towards more particles to increase pressure)
   d) no shift (forward & reverse rates increase equally)

(more on next page)

3. $2CO_{(g)} + O_{2(g)} \leftrightarrows 2CO_{2(g)} + 566kJ$

a) increase $[CO_2]$

b) decrease $[CO]$

c) increase the pressure by adding $He_{(g)}$

d) raise the temperature

solution:

a) shift left / to reactants

b) shift left / to reactants

c) no shift (He is a noble gas and will not react with anything, thus it will not directly effect the concentrations of reactants or products. While the pressure of the overall system increases, the ***concentrations*** *– in terms of moles per litre – of the reactant and product molecules do not change, therefore there is no change in forward or reverse reaction rates. Talk to your teacher about this if you want further clarification.)*

d) shift left / to reactants

4. $2Hg_{(l)} + O_{2(g)} \leftrightarrows 2HgO_{(s)}$ $\Delta H = -90.8kJ/mol$

a) increase $[O_2]$

b) add more $Hg_{(l)}$

c) increase the surface area of the $HgO_{(s)}$

d) raise the temperature

solution:

a) shift right / to products

b) no shift (addition of a pure liquid doesn't change any concentrations)

c) no shift (forward & reverse rates increase equally)

d) shift left / to reactants

(more on next page)

5. $N_{2(g)} + 3H_{2(g)} \leftrightarrows 2NH_{3(g)}$ $\Delta H = -91.8 kJ/mol$

a) increase $[N_2]$
b) increase $[H_2]$
c) increase the volume
d) lower the temperature
e) add a catalyst
f) remove NH_3 by dissolving it in water

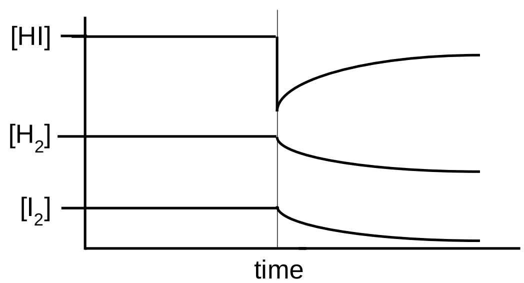
solution:

a) shift right / to products
b) shift right / to products
c) shift left / to reactants (towards more particles to increase pressure)
d) shift right / to products (to add heat to the system)
e) no shift (forward & reverse rates increase equally)
f) shift right / to products

6. Interpret each graph in terms of the changes that have been imposed on the equilibrium.

$H_{2(g)} + I_{2(g)} \leftrightarrows 2HI_{(g)}$ $\Delta H = +52.7 kJ/mol$

a)



solution:

The sudden drop in [HI] indicates that some of it has been removed. This decrease in [product] results in a shift right (towards the products) resulting in a decrease in $[H_2]$ and $[I_2]$ and an increase in [HI] until equilibrium is re-established.

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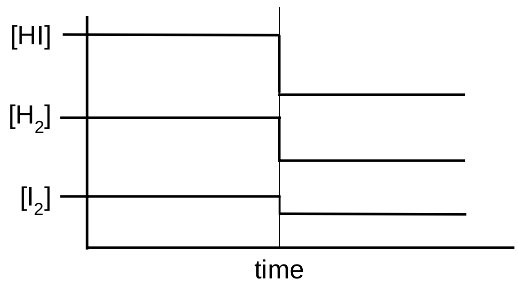
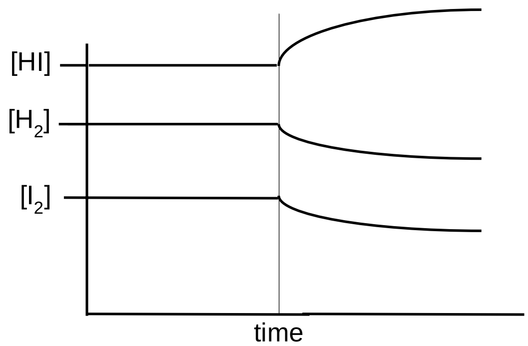
b)



solution:

The sudden drop in all concentrations indicates that overall system pressure has decreased (perhaps due to an increase in volume). Because there are an equal number of particles on both the product and reactant side, no shift will occur as shifting either way will ***not*** *increase the pressure to counteract the stress.*

c)



solution:

There is no sudden change in any concentration, so nothing has been removed or added and pressure has not changed. Catalysts and surface area do not affect equilibrium position shifts, so the only remaining possible factor is temperature. This is an endothermic reaction, an increase in product concentration with a decrease in reactant would indicate that the temperature was increased, shifting the equilibrium away from the side the heat term is on.

KEY – Unit 2 Problem Set C – KEY

1. A 1.0L reaction vessel contained 0.750mol of $CO_{(g)}$ and 0.275mol of $H_2O_{(g)}$. After 1.0h, equilibrium was reached. Analysis showed that 0.25mol of $CO_{2(g)}$ was present. The equation for the reaction is:

$$CO_{(g)} + H_2O_{(g)} \leftrightarrows CO_{2(g)} + H_{2(g)}$$

Find K_{eq} for the reaction.

solution:

bold *numbers in the ICE table come from information in the question.*

	CO	+	H_2O	⇆	CO_2	+	H_2
I	***0.750***		***0.275***		***0***		***0***
C	*-0.25*		*-0.25*		*+0.25*		*+0.25*
E	*0.50*		*0.025*		***0.25***		*0.25*

$$K_{eq} = \frac{[CO_2][H_2]}{[CO][H_2O]}$$

$$= \frac{[0.25][0.25]}{[0.50][0.025]}$$

$$K_{eq} = 5.0$$

2. A 5.0L reaction vessel was initially filled with 6.0mol of SO_2, 2.5mol of NO_2 and 1.0mol of SO_3. After equilibrium was reached, the vessel was found to contain 3.0mol of SO_3. Calculate K_{eq} for the equation:

$$SO_{2(g)} + NO_{2(g)} \leftrightarrows SO_{3(g)} + NO_{(g)}$$

solution:

bold *numbers in the ICE table come from information in the question. The container is stated to be 10L, so remember to calculate concentrations based on that.*

	SO_2	+	NO_2	⇆	SO_3	+	NO
I	***1.2***		***0.50***		***0.20***		***0***
C	*-0.40*		*-0.40*		*+0.40*		*+0.40*
E	*0.8*		*0.10*		***0.60***		*0.40*

$$K_{eq} = \frac{[SO_3][NO]}{[SO_2][NO_2]}$$

$$= \frac{[0.60][0.40]}{[0.80][0.10]}$$

$$K_{eq} = 3.0$$

3. Consider the equilibrium:

$$3I_{2(g)} + 4F_{2(g)} \leftrightarrows 2IF_{3(g)} + I_4F_{2(g)}$$

At a certain temperature 3.0mol of F_2 and 2.0mol of I_2 are introduced into a 10.0L container. At equilibrium the concentration of I_4F_2 is 0.020mol/L. Calculate K_{eq} for the reaction.

solution:

Bold *numbers in the ICE table come from information in the question. The container is stated to be 10L, so remember to calculate concentrations based on that.*

	$3I_2$	+	$4F_2$	⇆	$2IF_3$	+	I_4F_2
I	**0.20**		**0.30**		**0**		**0**
C	-0.060		-0.080		+0.040		+0.020
E	0.14		0.22		0.040		**0.020**

$$K_{eq} = \frac{[IF_3]^2[I_4F_2]}{[I_2]^3[F_2]^4}$$

$$= \frac{[0.040]^2[0.020]}{[0.14]^3[0.22]^4}$$

$$= 4.9782$$

K_{eq} = 5.0 *(rounded to correct sig. figs.)*

4. At a certain temperature, $K_{eq} = 4$ for the reaction:

$$2HF_{(g)} \leftrightarrows H_{2(g)} + F_{2(g)}$$

Predict the direction of shift of the equilibrium, if any, that will occur when the following systems are introduced into a 1.00L reaction vessel.

a) 0.60mol of HF, 0.40mol of H_2 and 0.80mol of F_2

b) 0.040mol of HF, 0.10mol of H_2 and 0.12mol of F_2

c) 0.060mol of HF, 0.36mol of H_2 and 0.040mol of F_2

solution:

a)

$$Q = \frac{[H_2][F_2]}{[HF]^2}$$

$$= \frac{[0.40][0.80]}{[0.60]^2}$$

$$= 0.89$$

$Q < K_{eq}$ ∴ *shift to product*

b)

$$Q = \frac{[H_2][F_2]}{[HF]^2}$$

$$= \frac{[0.10][0.12]}{[0.040]^2}$$

$$= 7.5$$

$Q > K_{eq}$ ∴ *shift to reactant*

c)

$$Q = \frac{[H_2][F_2]}{[HF]^2}$$

$$= \frac{[0.36][0.040]}{[0.060]^2}$$

$$= 4.0$$

$Q = K_{eq}$ ∴ *no shift*

5. At a certain temperature, K_{eq} = 55 for the reaction:

$$2O_{3(g)} \rightleftarrows 3O_{2(g)}$$

Predict the direction of the net reaction, if any, that will occur when the following systems are introduced into a 10L reaction vessel.

a) 0.700mol of O_3 and 3.00mol of O_2

b) 0.0060mol of O_3 and 0.70mol of O_2

c) 1.20mol of O_3 and 2.90mol of O_2

solution:

a)

$$Q = \frac{[O_2]^3}{[O_3]^2} = \frac{[0.300]^3}{[0.0700]^2} = 5.51$$

$Q < K_{eq}$ ∴ *shift to product*

b)

$$Q = \frac{[O_2]^3}{[O_3]^2} = \frac{[0.070]^3}{[0.00060]^2} = 950$$

$Q > K_{eq}$ ∴ *shift to reactant*

c)

$$Q = \frac{[O_2]^3}{[O_3]^2} = \frac{[0.290]^3}{[0.120]^2} = 1.69$$

$Q < K_{eq}$ ∴ *shift to product*

6. At a certain temperature, K_{eq} = 100 for the reaction:

$$CH_{4(g)} + 2H_2S_{(g)} \leftrightarrows CS_{2(g)} + 4H_{2(g)}$$

Some CH_4 and H_2S were introduced into a 1.0L container and at equilibrium 0.10mol of CH_4 and 0.30mol of H_2S were found. What was $[CS_2]$ at equilibrium?

solution:

Bold *numbers in the ICE table come from information in the question.*

	CH_4	+	$2H_2S$	⇆	CS_2	+	$4H_2$
I					*0*		*0*
C					+*x*		+*4x*
E	***0.10***		***0.30***		*x*		*4x*

$$K_{eq} = \frac{[CS_2][H_2]^4}{[CH_4][H_2S]^2}$$

$$100 = \frac{(x)(4x)^4}{(0.10)(0.30)^2}$$

$$100 = \frac{256x^5}{0.009}$$

$$x = \sqrt[5]{\frac{0.90}{256}}$$

$$x = 0.32$$

$[CS_2]$ at equilibrium is 0.32M

7. A reaction mixture,

$$CO_{(g)} + H_2O_{(g)} \leftrightarrows CO_{2(g)} + H_{2(g)}$$

when at equilibrium, contains 0.20mol of H_2, 0.70mol of CO_2, 0.20mol of CO and 0.30mol of H_2O in a 1.0L reaction vessel. How much CO_2 would have to be added to raise the amount of CO to 0.30mol?

solution:

Bold *numbers in the ICE table come from information in the question.*

The "+x" indicates the unknown amount of CO_2 added.

	CO	+	*H₂0*	⇆	*CO₂*	+	*H₂*
I	***0.20***		***0.30***		***0.70+x***		***0.20***
C	*+0.10*		*+0.10*		*-0.10*		*-0.10*
E	***0.30***		*0.40*		*0.60+x*		*0.10*

First, find the K_{eq} for the reaction based on the initial equilibrium state:

$$K_{eq} = \frac{[CO_2][H_2]}{[CO][H_2O]}$$

$$= \frac{(0.70)(0.20)}{(0.20)(0.30)}$$ *(don't use the "+x" here it is added "after")*

$$= 2.33$$ *(from initial data – OK to keep "extra" sig figs here, round at final answer)*

Then, use the K_{eq} to calculate the unknown for the final equilibrium:

$$K_{eq} = \frac{[CO_2][H_2]}{[CO][H_2O]}$$

$$2.33 = \frac{(0.60 + x)(0.10)}{(0.30)(0.40)}$$

$$2.33(0.30)(0.40) = (0.60 + x)(0.10)$$

$$2.8 = (0.60 + x)$$

$$2.2 = x$$

2.2 moles CO_2 would have to be added to raise the amount of CO to 0.30mol

8. When 1.00 mol of $HBr_{(g)}$ is placed in a 1.00L flask at 510°C the following equilibrium is achieved:

$$2HBr_{(g)} \leftrightarrows H_{2(g)} + Br_{2(g)}$$

At equilibrium, 0.14 mol of $H_{2(g)}$ is present. Calculate the value of K_{eq}.

solution:

Bold *numbers in the ICE table come from information in the question.*

	$2HBr$	$\leftrightarrows$	H_2	+	Br_2
I	***1.00***		*0*		*0*
C	*-0.28*		*+0.14*		*+0.14*
E	*0.72*		***0.14***		*0.14*

$$K_{eq} = \frac{[H_2][Br_2]}{[HBr]^2}$$

$$= \frac{(0.14)(0.14)}{(0.72)^2}$$

$$= 0.038$$

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