

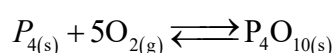
## QUIZ CH102 Basic Chemical Equilibrium

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### ► PROBLEMS

#### ► Problem 1

What is the equilibrium constant for the following reaction?



A)  $K_c = \frac{1}{[O_2]^5}$

B)  $K_c = [O_2]^5$

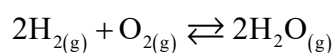
C)  $K_c = \frac{[P_4O_{10}]}{[P_4][O_2]^5}$

D)  $K_c = \frac{[P_4O_{10}]}{5[P_4][O_2]}$

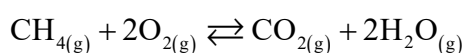
#### ► Problem 2

Calculate the equilibrium constant of the following reactions at 25°C. Refer to the Gibbs free energy data in the Additional Information section.

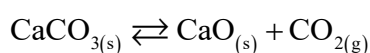
**Reaction 1:** Combustion of gaseous hydrogen.



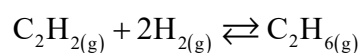
**Reaction 2:** Combustion of methane.



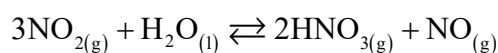
**Reaction 3:** Decomposition of limestone.



**Reaction 4:** Hydrogenation of acetylene to ethane.



**Reaction 5:** Final step in the industrial production of nitric acid.

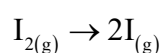


In the following table, associate each reaction number with the appropriate value of  $K$ .

Reaction No.	$K$
	$1.43 \times 10^{-23}$
	$1.78 \times 10^9$
	$2.70 \times 10^{42}$
	$2.21 \times 10^{80}$
	$1.89 \times 10^{140}$

#### → Problem 3.1

The reaction

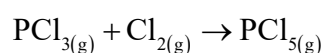


has an equilibrium constant of 6.8 at 1000 K. Calculate the reaction Gibbs free energy when the partial pressures of  $I_2$  and  $I$  are 0.12 bar and 0.95 bar, respectively. Under these conditions, what is the spontaneous direction of the reaction?

- α)** The forward reaction is spontaneous.
- β)** The back reaction is spontaneous.
- γ)** There is not enough information.

### → Problem 3.2

The reaction

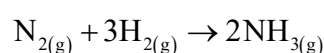


has an equilibrium constant of 49 at 500 K. Calculate the reaction Gibbs free energy when the partial pressures of  $\text{PCl}_3$ ,  $\text{Cl}_2$ , and  $\text{PCl}_5$  are 0.12 bar, 0.5 bar, and 1.41 bar, respectively. Under these conditions, what is the spontaneous direction of the reaction?

- α)** The forward reaction is spontaneous.
- β)** The back reaction is spontaneous.
- γ)** There is not enough information.

### → Problem 3.3

The reaction

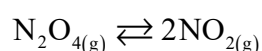


has an equilibrium constant of 41 at 400 K. Calculate the reaction Gibbs free energy when the partial pressures of  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{NH}_3$  are 4.0 bar, 1.6 bar, and 20 bar, respectively. Under these conditions, what is the spontaneous direction of the reaction?

- α)** The forward reaction is spontaneous.
- β)** The back reaction is spontaneous.
- γ)** There is not enough information.

### → Problem 4.1

For the reaction equilibrium at a temperature of 25°C,

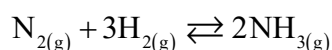


the concentrations of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  at equilibrium are  $5 \times 10^{-2}$  mol/L and  $1.2 \times 10^{-2}$  mol/L, respectively. The equilibrium constant for this reaction is:

- A)**  $K_c = 1.44 \times 10^{-4}$  M
- B)**  $K_c = 2.88 \times 10^{-4}$  M
- C)**  $K_c = 1.44 \times 10^{-3}$  M
- D)**  $K_c = 2.88 \times 10^{-3}$  M

### → Problem 4.2

For the reaction equilibrium at a temperature of 400 K,

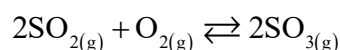


the concentrations of  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{NH}_3$  at equilibrium are  $1.2 \times 10^{-3}$  mol/L,  $3.6 \times 10^{-3}$  mol/L, and  $4.8 \times 10^{-5}$  mol/L, respectively. The equilibrium constant for this reaction is:

- A)**  $K_c = 0.412 \text{ M}^{-2}$
- B)**  $K_c = 4.12 \text{ M}^{-2}$
- C)**  $K_c = 41.2 \text{ M}^{-2}$
- D)**  $K_c = 412 \text{ M}^{-2}$

### → Problem 4.3

For the reaction equilibrium at a temperature of 500 K,

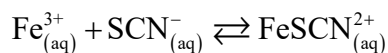


the concentrations of  $\text{SO}_2$ ,  $\text{O}_2$ , and  $\text{SO}_3$  at equilibrium are  $2.4 \times 10^{-5}$  mol/L,  $1.2 \times 10^{-5}$  mol/L, and  $1.3 \times 10^{-2}$  mol/L, respectively. The equilibrium constant for this reaction is:

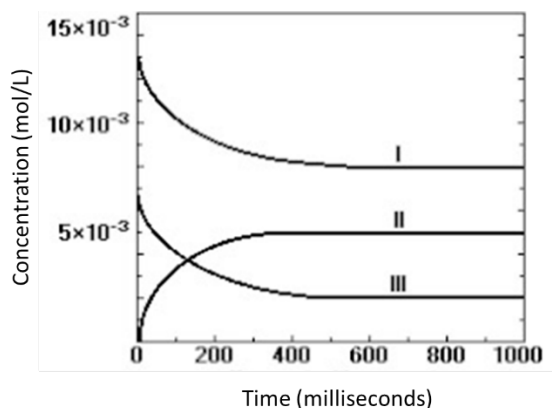
- A)**  $K_c = 2.45 \times 10^8 \text{ M}^{-1}$
- B)**  $K_c = 2.45 \times 10^{10} \text{ M}^{-1}$
- C)**  $K_c = 2.45 \times 10^{12} \text{ M}^{-1}$
- D)**  $K_c = 2.45 \times 10^{14} \text{ M}^{-1}$

### → Problem 4.4

The reaction of iron (III) ions with thiocyanate ions is represented by the chemical equilibrium



In one experiment involving this reaction, the concentration of ions varied in accordance with the following graph, where curves I, II and III correspond to  $\text{Fe}^{3+}$ ,  $\text{FeSCN}^{2+}$ , and  $\text{SCN}^{-}$ , respectively.



Determine the equilibrium constant for the formation of  $\text{FeSCN}^{2+}$  ions.

- A)  $K_c = 0.313 \text{ M}^{-1}$
- B)  $K_c = 3.13 \text{ M}^{-1}$
- C)  $K_c = 31.3 \text{ M}^{-1}$
- D)  $K_c = 313 \text{ M}^{-1}$

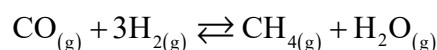
### → Problem 4.5

In a gas-phase equilibrium mixture of  $\text{H}_2$ ,  $\text{Cl}_2$  and  $\text{HCl}$  at 1000 K,  $[\text{H}_2] = 5.1 \times 10^{-7} \text{ mol/L}$  and  $[\text{HCl}] = 1.4 \times 10^{-2} \text{ mol/L}$ . Knowing that  $K_c$  at this temperature is  $4.8 \times 10^8$ , determine the equilibrium concentration of chlorine gas.

- A)  $[\text{Cl}_2] = 8.01 \times 10^{-7} \text{ M}$
- B)  $[\text{Cl}_2] = 3.12 \times 10^{-6} \text{ M}$
- C)  $[\text{Cl}_2] = 8.01 \times 10^{-6} \text{ M}$
- D)  $[\text{Cl}_2] = 3.12 \times 10^{-5} \text{ M}$

### → Problem 4.6

A gaseous mixture at 1200 K contains 0.36 mol  $\text{CO}$ , 0.12 mol  $\text{H}_2$  and 0.24 mol  $\text{H}_2\text{O}$ , plus an unknown amount of  $\text{CH}_4$  in each liter. The equilibrium in question is



Knowing that the equilibrium constant  $K_c = 4$ , find the equilibrium concentration of  $\text{CH}_4$ .

- A)  $[\text{CH}_4] = 1.04 \times 10^{-2} \text{ M}$
- B)  $[\text{CH}_4] = 6.04 \times 10^{-2} \text{ M}$
- C)  $[\text{CH}_4] = 0.104 \text{ M}$
- D)  $[\text{CH}_4] = 0.604 \text{ M}$

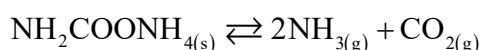
### → Problem 4.7

In a gas-phase equilibrium mixture of  $\text{PCl}_5$ ,  $\text{PCl}_3$ , and  $\text{Cl}_2$  at 500 K,  $p(\text{PCl}_5) = 1.2 \text{ bar}$  and  $p(\text{Cl}_2) = 5.4 \text{ bar}$ . Knowing that  $K_p$  at this temperature is 25, what is the partial pressure of  $\text{PCl}_3$ ?

- A)  $p(\text{PCl}_3) = 1.12 \text{ bar}$
- B)  $p(\text{PCl}_3) = 3.45 \text{ bar}$
- C)  $p(\text{PCl}_3) = 5.56 \text{ bar}$
- D)  $p(\text{PCl}_3) = 7.12 \text{ bar}$

## → Problem 5.1

The following equilibrium takes place at a temperature of 27°C and a total system pressure of 6 atm.

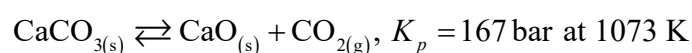


The ratio of the equilibrium constant in terms of partial pressures to the equilibrium constant in terms of molar concentrations is:

- A)  $K_p/K_c = (0.082 \times 27)^2$
- B)  $K_p/K_c = (0.082 \times 27)^3$
- C)  $K_p/K_c = (0.082 \times 300)^2$
- D)  $K_p/K_c = (0.082 \times 300)^3$

## → Problem 5.2

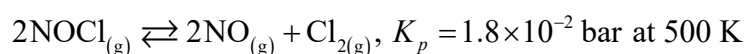
Determine the concentration-based equilibrium constant  $K_c$  for the following reaction:



- A)  $K_c = 0.187 \text{ M}$
- B)  $K_c = 1.87 \text{ M}$
- C)  $K_c = 18.7 \text{ M}$
- D)  $K_c = 187 \text{ M}$

## → Problem 5.3

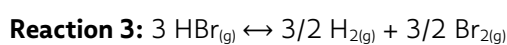
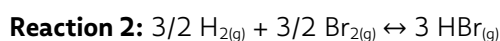
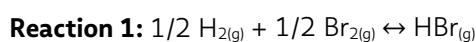
Determine the concentration-based equilibrium constant  $K_c$  for the following reaction:



- A)  $K_c = 4.33 \times 10^{-4} \text{ M}$
- B)  $K_c = 4.33 \times 10^{-3} \text{ M}$
- C)  $K_c = 4.33 \times 10^{-2} \text{ M}$
- D)  $K_c = 0.433 \text{ M}$

## → Problem 6.1

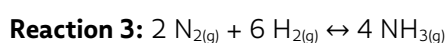
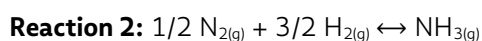
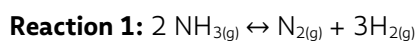
For the reaction  $\text{H}_{2(g)} + \text{Br}_{2(g)} \leftrightarrow 2 \text{HBr}_{(g)}$ ,  $K_c = 1.3 \times 10^{10}$  at 500 K. Using this information, find the value of  $K_c$  for each of the following reactions at the same temperature.



Reaction 1	Reaction 2	Reaction 3
A) $K_1 = 1.14 \times 10^5$	A) $K_2 = 1.01 \times 10^{14}$	A) $K_3 = 6.76 \times 10^{-17}$
B) $K_1 = 2.28 \times 10^5$	B) $K_2 = 1.48 \times 10^{14}$	B) $K_3 = 9.98 \times 10^{-17}$
C) $K_1 = 1.14 \times 10^6$	C) $K_2 = 1.01 \times 10^{15}$	C) $K_3 = 6.76 \times 10^{-16}$
D) $K_c = 2.28 \times 10^6$	D) $K_2 = 1.48 \times 10^{15}$	D) $K_3 = 9.98 \times 10^{-16}$

## → Problem 6.2

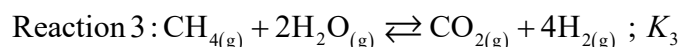
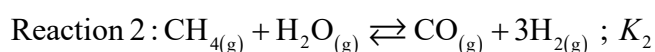
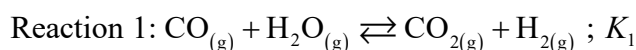
For the reaction  $\text{N}_{2(g)} + 3 \text{H}_{2(g)} \leftrightarrow 2 \text{NH}_{3(g)}$ ,  $K_c = 41$  at 400 K. Using this information, find the value of  $K_c$  for each of the following reactions at the same temperature.



Reaction 1	Reaction 2	Reaction 3
A) $K_1 = 1.22 \times 10^{-2}$	A) $K_2 = 3.20$	A) $K_3 = 1.68 \times 10^2$
B) $K_1 = 2.44 \times 10^{-2}$	B) $K_2 = 6.40$	B) $K_3 = 3.36 \times 10^2$
C) $K_1 = 0.122$	C) $K_2 = 12.8$	C) $K_3 = 1.68 \times 10^3$
D) $K_1 = 0.244$	D) $K_2 = 25.6$	D) $K_3 = 3.36 \times 10^3$

### → Problem 6.3

Consider the following reactions.



Which of the following relations is correct?

- A)  $K_1\sqrt{K_2} = K_3$
- B)  $K_2K_3 = K_1$
- C)  $K_1K_2 = K_3$
- D)  $K_3K_2^3 = K_1^2$

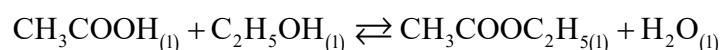
### → Problem 7.1

The equilibrium constant  $K_p$  for the reaction  $\text{N}_2\text{O}_{4(g)} \leftrightarrow 2\text{NO}_{2(g)}$  is 680 mmHg at 775 K. Calculate the percentage dissociation of  $\text{N}_2\text{O}_4$  at an equilibrium pressure of 180 mmHg and determine the pressure at which the dissociation will be 80%.

- A)  $x = 0.697$  and  $P = 47.8$  mmHg
- B)  $x = 0.697$  and  $P = 95.6$  mmHg
- C)  $x = 0.911$  and  $P = 47.8$  mmHg
- D)  $x = 0.911$  and  $P = 95.6$  mmHg

### → Problem 7.2

The reaction



has an equilibrium constant of 4.0 at a given temperature. 120 g of acetic acid and 92 g of ethanol are mixed in a cylinder with a volume of 1 L. The mole fraction of ester at equilibrium is:

- A)  $\chi_{\text{ester}} = 0.112$
- B)  $\chi_{\text{ester}} = 0.333$
- C)  $\chi_{\text{ester}} = 0.512$
- D)  $\chi_{\text{ester}} = 0.666$

### → Problem 7.3

A cylinder holds a mixture of  $\text{N}_2$ ,  $\text{H}_2$  and  $\text{NH}_3$ . Initially, the partial pressures of nitrogen, hydrogen, and ammonia are 1 atm, 3 atm, and zero, respectively. Once equilibrium is attained, the total system pressure is found to be 3 atm. Under these conditions, the equilibrium constant for the formation of ammonia is:

- A)  $K_p = 2.41 \times 10^{-2} \text{ atm}^{-2}$
- B)  $K_p = 0.114 \text{ atm}^{-2}$
- C)  $K_p = 0.593 \text{ atm}^{-2}$
- D)  $K_p = 1.14 \text{ atm}^{-2}$

### → Problem 7.4

The reaction equilibrium  $\text{AB}_{2(g)} \leftrightarrow \text{AB}_{(g)} + \text{B}_{(g)}$  is such that the initial pressure of  $\text{AB}_2$  is 500 torr, while those of  $\text{AB}$  and  $\text{B}$  are both zero. The equilibrium pressure of the system is 600 torr. The equilibrium constant is then:

- A)  $K_p = 6.25$  torr
- B)  $K_p = 12.5$  torr
- C)  $K_p = 25$  torr
- D)  $K_p = 50$  torr

### → Problem 7.5

In a mixture of  $\text{PCl}_5$ ,  $\text{PCl}_3$  and  $\text{Cl}_2$  at a total pressure of 5 atm,  $\text{PCl}_5$  is 15% dissociated. Determine the system pressure at which  $\text{PCl}_5$  will be 30% dissociated, all else being equal.

- A)  $P = 1.16$  atm
- B)  $P = 2.88$  atm
- C)  $P = 3.44$  atm
- D)  $P = 4.56$  atm

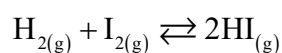
### → Problem 7.6

At 25°C and 1 atmospheric pressure, the partial pressures in an equilibrium mixture of gaseous  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  are 0.8 and 0.4 atm, respectively. Calculate the partial pressures of these gases when they are in equilibrium at 25°C and a total pressure of 10 atm.

- A)  $p(\text{N}_2\text{O}_4) = 5.52$  atm and  $p(\text{NO}_2) = 4.48$  atm
- B)  $p(\text{N}_2\text{O}_4) = 8.68$  atm and  $p(\text{NO}_2) = 1.32$  atm
- C)  $p(\text{N}_2\text{O}_4) = 4.48$  atm and  $p(\text{NO}_2) = 5.52$  atm
- D)  $p(\text{N}_2\text{O}_4) = 1.32$  atm and  $p(\text{NO}_2) = 8.68$  atm

### → Problem 7.7

Consider the reaction



At equilibrium,  $[\text{H}_2] = 0.5$  M,  $[\text{I}_2] = 0.5$  M and  $[\text{HI}] = 1.23$  M in a 1-L cylinder. If 0.6 mole of HI is removed, what will be the equilibrium composition?

### → Problem 7.8

At 800 K a reaction mixture contained 0.5 mol of  $\text{SO}_2$ , 0.12 mol of  $\text{O}_2$ , and 5 mol of  $\text{SO}_3$  at equilibrium. At the temperature in question,  $K_c$  for the equilibrium  $2\text{SO}_{2(g)} + \text{O}_{2(g)} \leftrightarrow 2\text{SO}_{3(g)}$  is 900. The container in which the mixture is inserted has a volume of 1 liter. Calculate how much  $\text{O}_2$  should be added to the system in order to obtain 5.2 mol of  $\text{SO}_3$  at the same temperature.

- A)  $x = 0.02$  mol  $\text{O}_2$
- B)  $x = 0.08$  mol  $\text{O}_2$
- C)  $x = 0.2$  mol  $\text{O}_2$
- D)  $x = 0.8$  mol  $\text{O}_2$

### → Problem 7.9

An equilibrium mixture at 300 K contains  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  at 0.28 and 1.1 atm, respectively. If the volume of the container is doubled, all else being equal, calculate the new equilibrium pressure of the two gases.

- A)  $p(\text{N}_2\text{O}_4) = 0.095$  atm and  $p(\text{NO}_2) = 0.640$  atm
- B)  $p(\text{N}_2\text{O}_4) = 0.282$  atm and  $p(\text{NO}_2) = 0.453$  atm
- C)  $p(\text{N}_2\text{O}_4) = 0.640$  atm and  $p(\text{NO}_2) = 0.095$  atm
- D)  $p(\text{N}_2\text{O}_4) = 0.453$  atm and  $p(\text{NO}_2) = 0.282$  atm

### → Problem 8.1

$a$  moles of  $\text{PCl}_{5(g)}$  are heated in a closed cylinder and allowed to reach the typical equilibrium  $\text{PCl}_{5(g)} \leftrightarrow \text{PCl}_{3(g)} + \text{Cl}_{2(g)}$  at a pressure of  $P$  atm. If  $x$  moles of  $\text{PCl}_5$  dissociate at equilibrium, then:

A)  $\frac{x}{a} = \frac{K_p}{K_p + P}$

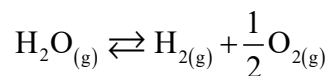
B)  $\frac{x}{a} = \left( \frac{K_p + P}{K_p} \right)^{1/2}$

C)  $\frac{x}{a} = \left( \frac{K_p}{P} \right)^{1/2}$

D)  $\frac{x}{a} = \left( \frac{K_p}{K_p + P} \right)^{1/2}$

## → Problem 8.2

Consider the equilibrium of water vapor,



If  $\alpha$  is the degree of dissociation at equilibrium pressure  $P$ , then  $K_p$  is given by:

A)  $K_p = \alpha^3 \left(\frac{P}{2}\right)^{1/2}$

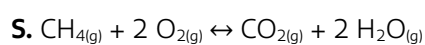
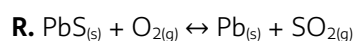
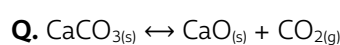
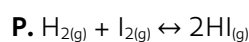
B)  $K_p = \frac{\alpha^3 P^{3/2}}{(1-\alpha)(2+\alpha)}$

C)  $K_p = \frac{\alpha^{3/2} P^{1/2}}{(1-\alpha)(2+\alpha)^{1/2}}$

D)  $K_p = \frac{\alpha^3 P^{1/2}}{(1+\alpha)(2-\alpha)^{1/2}}$

## → Problem 9.1

The following four reaction equilibria occur in a cylinder with a movable piston.

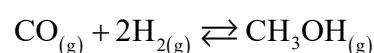


If the piston is slowly compressed, in which of these reactions will the equilibrium be displaced, be it favoring reactants or products?

- A) Reaction P only.
- B) Reactions R and Q only.
- C) Reactions P, Q and S only.
- D) Reaction Q only.

## → Problem 9.2

The synthesis of methanol from carbon monoxide and gaseous hydrogen can be represented by the chemical equilibrium

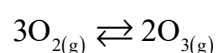


Knowing that the forward reaction is exothermic, which of the following adjustments would **not** favor the formation of methanol?

- A) Increasing the amount of hydrogen at constant volume.
- B) Increasing the system pressure by adding argon at constant volume.
- C) Cooling the system at constant volume.
- D) Reducing the system volume and consequently increasing pressure.

## → Problem 9.3

In the high atmosphere or in a lab, ozone can be formed by the endothermic reaction

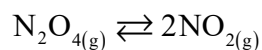


In order to favor the formation of ozone,

- A) Both temperature and pressure should be increased.
- B) The temperature should be increased and the pressure should be decreased.
- C) The temperature should be decreased and the pressure should be increased.
- D) Both temperature and pressure should be decreased.

### → Problem 9.4

The following chemical equilibrium was established in a cylinder with a mobile piston.



The following adjustments can be made to the system:

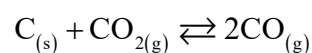
- P. Reducing the volume by compressing the piston.
- Q. Adding more gaseous  $\text{NO}_2$  to the system while the piston remains fixed.
- R. Adding more gaseous  $\text{N}_2\text{O}_4$  to the system while the piston remains fixed.
- S. Introducing gaseous argon to the system while the piston remains fixed.

Which of these adjustments would favor the back reaction, that is, the formation of  $\text{N}_2\text{O}_4$ ?

- A) P only.
- B) P and Q only.
- C) P, Q and R only.
- D) Q and S only.

### → Problem 9.5

The conversion of carbon dioxide into carbon monoxide at a given temperature can be represented by the reaction



The change in enthalpy of the forward reaction at a given temperature is  $\Delta H = 174 \text{ kJ/mol}$  carbon. The following adjustments can be made to the system:

- P. Increasing temperature.
- Q. Reducing pressure.
- R. Adding solid carbon to the system.
- S. Introducing a catalyst.

Which of these adjustments would favor the forward reaction, that is, the formation of  $\text{CO}$ ?

- A) P only.
- B) P and Q only.
- C) P, Q and R only.
- D) Q and S only.

### → Problem 10.1

The equilibrium constant  $K_p$  for  $\text{N}_2\text{O}_{4(g)} \leftrightarrow 2\text{NO}_{2(g)}$  is 0.15 at 298 K. Predict its value at 500 K. Use the enthalpy data in Table 2 and assume that the reaction enthalpy is constant over the temperature range of interest.

- A)  $K_p = 16.9$
- B)  $K_p = 1.69 \times 10^2$
- C)  $K_p = 1.69 \times 10^3$
- D)  $K_p = 1.69 \times 10^4$

### → Problem 10.2

The equilibrium constant  $K_p$  for  $\text{PCl}_{5(g)} \leftrightarrow \text{PCl}_{3(g)} + \text{Cl}_{2(g)}$  is 78.3 at 523 K. Predict its value at 800 K. Use the enthalpy data in Table 2 and assume that the reaction enthalpy is constant over the temperature range of interest.

- A)  $K_p = 8.58 \times 10^2$
- B)  $K_p = 8.58 \times 10^3$
- C)  $K_p = 8.58 \times 10^4$
- D)  $K_p = 8.58 \times 10^5$

### → Problem 10.3

The equilibrium constant  $K_p$  for  $2 \text{SO}_{3(g)} \leftrightarrow 2 \text{SO}_{2(g)} + \text{O}_{2(g)}$  is  $2.5 \times 10^{-25}$  at 298 K. Predict its value at 500 K. Use the enthalpy data in Table 2 and assume that the reaction enthalpy is constant over the temperature range of interest.

- A)  $K_p = 2.54 \times 10^{-11}$
- B)  $K_p = 2.54 \times 10^{-9}$
- C)  $K_p = 2.54 \times 10^{-7}$
- D)  $K_p = 2.54 \times 10^{-5}$



## ▶ ADDITIONAL INFORMATION

**Table 1.** Standard Gibbs free energy of formation for selected compounds

Compound	$\Delta G_f^\circ$ (kJ/mol)
$C_2H_2(g)$	+209.2
$C_2H_6(g)$	-32.8
$CaCO_3(s)$	-1128.8
$CaO(s)$	-604.0
$CH_4(g)$	-50.7
$CO_2(g)$	-394.4
$H_2O(g)$	-228.6
$H_2O(l)$	-237.1
$HNO_3(aq)$	-111.3
$NO(g)$	+86.6
$NO_2(g)$	+51.3

**Table 2.** Standard enthalpy of formation for selected compounds

Compound	$\Delta H_f^\circ$ (kJ/mol)
$N_2O_4(g)$	9.16
$NO_2(g)$	33.2
$PCl_3(g)$	-287.0
$PCl_5(g)$	-374.9
$SO_2(g)$	-296.8
$SO_3(g)$	-395.7

## ▶ SOLUTIONS

### P.1 → Solution

Solid compounds are not included in the expression for the equilibrium constant. The equilibrium constant for the reaction in question is simply  $K_c = 1/[O_2]^5$ .

♦ The correct answer is **A**.

### P.2 → Solution

**Part 1:** The equilibrium constant is related to the reaction Gibbs free energy by the simple law

$$\Delta G_r^\circ = -RT \ln K \rightarrow \ln K = -\frac{\Delta G_r^\circ}{RT}$$

Thus, calculating the standard change in Gibbs free energy should yield the equilibrium constant. For the reaction at hand,  $\Delta G_r^\circ$  is

$$\begin{aligned} \Delta G_r^\circ &= 2\Delta G_f^\circ [H_2O_{(g)}] - \Delta G_f^\circ [O_{2(g)}] - 2\Delta G_f^\circ [H_{2(g)}] \\ \therefore \Delta G_r^\circ &= 2 \times (-228.6) - 0 - 2 \times 0 = -457.2 \text{ kJ/mol} \end{aligned}$$

so that

$$\begin{aligned} \ln K &= -\frac{(-457,200)}{8.314 \times 298} = 185 \\ \therefore K &= e^{185} = \boxed{2.21 \times 10^{80}} \end{aligned}$$

**Part 2:** As stated above, the equilibrium constant can be obtained from the reaction Gibbs free energy,

$$\ln K = -\frac{\Delta G_r^\circ}{RT}$$

For the reaction in question, we have

$$\begin{aligned} \Delta G_r^\circ &= 2\Delta G_f^\circ [H_2O_{(g)}] + \Delta G_f^\circ [CO_{2(g)}] - 2\Delta G_f^\circ [O_{2(g)}] - \Delta G_f^\circ [CH_{4(g)}] \\ \therefore \Delta G_r^\circ &= 2 \times (-228.6) + (-394.4) - 2 \times 0 - (-50.7) = -800.9 \text{ kJ/mol} \end{aligned}$$

so that

$$\ln K = -\frac{(-800,900)}{8.314 \times 298} = 323$$

$$\therefore K = \exp(323) = \boxed{1.89 \times 10^{140}}$$

**Part 3:** The change in Gibbs free energy is

$$\ln K = -\frac{\Delta G_r^\circ}{RT}$$

For the reaction in question,  $\Delta G_r^\circ$  is

$$\Delta G_r^\circ = \Delta G_f^\circ [\text{CO}_{2(g)}] + \Delta G_f^\circ [\text{CaO}_{(s)}] - \Delta G_f^\circ [\text{CaCO}_{3(s)}]$$

$$\therefore \Delta G_r^\circ = -394.4 + (-604.0) - (-1128.8) = 130.4 \text{ kJ/mol}$$

so that

$$\ln K = -\frac{\Delta G_r^\circ}{RT} = -\frac{130,400}{8.314 \times 298} = -52.6$$

$$\therefore K = e^{-52.6} = \boxed{1.43 \times 10^{-23}}$$

**Part 4:** The standard Gibbs free energy for this reaction is

$$\Delta G_r^\circ = \Delta G_f^\circ [\text{C}_2\text{H}_{6(g)}] - 2\Delta G_f^\circ [\text{H}_{2(g)}] - \Delta G_f^\circ [\text{C}_2\text{H}_{2(g)}]$$

$$\therefore \Delta G_r^\circ = -32.8 - 2 \times 0 - 209.2 = -242 \text{ kJ/mol}$$

and the equilibrium constant follows as

$$\ln K = -\frac{\Delta G_r^\circ}{RT} = -\frac{(-242,000)}{8.314 \times 298} = 97.7$$

$$\therefore K = \exp(97.7) = \boxed{2.70 \times 10^{42}}$$

**Part 5:** The standard Gibbs free energy for this reaction is

$$\Delta G_r^\circ = \Delta G_f^\circ [\text{NO}_{(g)}] + 2\Delta G_f^\circ [\text{HNO}_{3(g)}] - \Delta G_f^\circ [\text{H}_2\text{O}_{(l)}] - 3\Delta G_f^\circ [\text{NO}_{2(g)}]$$

$$\therefore \Delta G_r^\circ = 86.6 + 2 \times (-111.3) - (-237.1) - 3 \times (51.3) = -52.8 \text{ kJ/mol}$$

and the equilibrium constant follows as

$$\ln K = -\frac{\Delta G_r^\circ}{RT} = -\frac{(-52,800)}{8.314 \times 298} = 21.3$$

$$\therefore K = e^{21.3} = \boxed{1.78 \times 10^9}$$

In the following table, the reactions are assigned to the corresponding values of  $K$ .

Reaction No.	$K$
3	$1.43 \times 10^{-23}$
5	$1.78 \times 10^9$
4	$2.70 \times 10^{42}$
1	$2.21 \times 10^{80}$
2	$1.89 \times 10^{140}$

### P.3 → Solution

**Part 1:** The free energy at a specific set of conditions is given by

$$\Delta G_r = \Delta G_r^\circ + RT \ln Q$$

where  $\Delta G_r^\circ = -RT \ln K$ , with the result that

$$\Delta G_r = -RT \ln K + RT \ln Q = -RT \ln K + RT \ln \frac{p(I)^2}{p(I_2)}$$

$$\therefore \Delta G_r = -8.314 \times 1000 \times \ln 6.8 + 8.314 \times 1000 \times \ln \frac{0.95^2}{0.12} = +0.838 \text{ kJ/mol}$$

Because  $\Delta G_r$  is greater than zero, the reverse reaction is spontaneous.

◆ The correct answer is **β**.

**Part 2:** The free energy at a specific set of conditions is expressed as

$$\Delta G_r = \Delta G_r^\circ + RT \ln Q$$

where  $\Delta G_r^\circ = -RT \ln K$ , so that

$$\Delta G_r = -RT \ln K + RT \ln Q = -RT \ln K + RT \ln \frac{p(\text{PCl}_5)}{p(\text{PCl}_3)p(\text{Cl}_2)}$$

$$\therefore \Delta G_r = -8.314 \times 500 \times \ln 49 + 8.314 \times 500 \times \ln \frac{1.41}{0.12 \times 0.5} = -3.05 \text{ kJ/mol}$$

Because  $\Delta G_r$  is lower than zero, the forward reaction is spontaneous.

◆ The correct answer is **α**.

**Part 3:** The reaction Gibbs free energy can be determined with the same formula used in the previous parts, namely

$$\Delta G_r = -RT \ln K + RT \ln Q = -RT \ln K + RT \ln \frac{p(\text{NH}_3)^2}{p(\text{N}_2)p(\text{H}_2)^3}$$

$$\therefore \Delta G_r = -8.314 \times 400 \times \ln 41 + 8.314 \times 400 \times \ln \left( \frac{20^2}{4.0 \times 1.6^3} \right) = -1.72 \text{ kJ/mol}$$

Because  $\Delta G_r$  is lower than zero, the forward reaction is spontaneous.

◆ The correct answer is **α**.

## P.4 → Solution

**Part 1:** From the law of mass action, the equilibrium constant is determined to be

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{0.012^2}{0.05} = \boxed{2.88 \times 10^{-3} \text{ M}}$$

◆ The correct answer is **D**.

**Part 2:** From the law of mass action, the equilibrium constant is calculated to be

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(4.8 \times 10^{-5})^2}{(1.2 \times 10^{-3}) \times (3.6 \times 10^{-3})^3} = \boxed{41.2 \text{ M}^{-2}}$$

◆ The correct answer is **C**.

**Part 3:** From the law of mass action, the equilibrium constant is calculated as

$$K = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} = \frac{(1.3 \times 10^{-2})^2}{(2.4 \times 10^{-5})^2 \times (1.2 \times 10^{-5})} = \boxed{2.45 \times 10^{10} \text{ M}^{-1}}$$

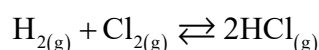
◆ The correct answer is **B**.

**Part 4:** Inspecting the graph, we see that the concentrations of  $\text{Fe}^{3+}$ ,  $\text{FeSCN}^{2+}$  and  $\text{SCN}^-$  plateau at  $8 \times 10^{-3} \text{ mol/L}$ ,  $5 \times 10^{-3} \text{ mol/L}$ , and  $2 \times 10^{-3} \text{ mol/L}$ , respectively. Invoking the law of mass action, we have

$$K_c = \frac{[\text{FeSCN}^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^-]} = \frac{5 \times 10^{-3}}{(8 \times 10^{-3}) \times (2 \times 10^{-3})} = \boxed{313 \text{ M}^{-1}}$$

◆ The correct answer is **D**.

**Part 5:** The equilibrium reaction in question is



The missing concentration can be easily determined with the law of mass action,

$$K_c = \frac{[\text{HCl}]^2}{[\text{H}_2][\text{Cl}_2]} \rightarrow [\text{Cl}_2] = \frac{1}{K_c} \frac{[\text{HCl}]^2}{[\text{H}_2]}$$

$$\therefore [\text{Cl}_2] = \frac{1}{4.8 \times 10^8} \times \frac{(1.4 \times 10^{-2})^2}{(5.1 \times 10^{-7})} = \boxed{8.01 \times 10^{-7} \text{ M}}$$

◆ The correct answer is **A**.

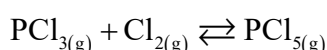
**Part 6:** Appealing to the law of mass action, we have

$$K_c = \frac{[\text{CH}_4][\text{H}_2\text{O}]}{[\text{CO}][\text{H}_2]^3} \rightarrow [\text{CH}_4] = K_c \frac{[\text{CO}][\text{H}_2]^3}{[\text{H}_2\text{O}]}$$

$$\therefore [\text{CH}_4] = 4.0 \times \frac{0.36 \times 0.12^3}{0.24} = \boxed{1.04 \times 10^{-2} \text{ M}}$$

◆ The correct answer is **A**.

**Part 7:** The equilibrium reaction for this system is



From the law of mass action, we have

$$K = \frac{p(\text{PCl}_3)p(\text{Cl}_2)}{p(\text{PCl}_5)} \rightarrow p(\text{PCl}_3) = K \times \frac{p(\text{PCl}_5)}{p(\text{Cl}_2)}$$

$$\therefore p(\text{PCl}_3) = 25 \times \frac{1.2}{5.4} = \boxed{5.56 \text{ bar}}$$

◆ The correct answer is **C**.

## P.5 → Solution

**Part 1:** The ratio of the pressure-based equilibrium constant to the concentration-based equilibrium constant is

$$\frac{K_p}{K_c} = (RT)^{\Delta n}$$

Here, the gas constant  $R = 0.082$  involves temperature units in degrees Kelvin, so the temperature must be specified accordingly; for the system at hand,  $T = 27^\circ\text{C} = 300 \text{ K}$ . The ratio also involves the variation in moles of gas,  $\Delta n$ . In the present system, the products side has  $2 + 1 = 3$  volume-equivalents of gas, while the reactants side has zero; it follows that  $\Delta n = 3 - 0 = 3$ . Thus, the ratio of equilibrium constants is

$$\frac{K_p}{K_c} = \boxed{(0.082 \times 300)^3}$$

◆ The correct answer is **D**.

**Part 2:** Constants  $K_p$  and  $K_c$  are related as

$$K_p = (RT)^{\Delta n} K_c$$

For the reaction in question,  $\Delta n = 1$ . In addition,  $R = 8.314 \times 10^{-2}$  for pressure and volume expressed in bars and liters, respectively, so that

$$K_p = (RT)^{\Delta n} K_c \rightarrow K_c = \frac{K_p}{(RT)^{\Delta n}}$$

$$\therefore K_c = \frac{167}{[(8.314 \times 10^{-2}) \times 1073]^1} = \boxed{1.87 \text{ M}}$$

◆ The correct answer is **B**.

**Part 3:** Noting that  $R = 8.314 \times 10^{-2} \text{ L}\cdot\text{bar}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  and  $\Delta n = 3 - 2 = 1$ , it follows that

$$K = (RT)^{\Delta n} K_c \rightarrow K_c = \frac{K}{(RT)^{\Delta n}}$$

$$\therefore K_c = \frac{1.8 \times 10^{-2}}{[(8.314 \times 10^{-2}) \times 500]^1} = \boxed{4.33 \times 10^{-4} \text{ M}}$$

◆ The correct answer is **A**.

### P.6 → Solution

**Part 1:** Reaction 1 is the forward reaction of hydrogen bromide formation, only with half the stoichiometric coefficients. Accordingly, the equilibrium constant is

$$K_1 = K^{1/2} = (1.3 \times 10^{10})^{1/2} = \boxed{1.14 \times 10^5}$$

Reaction 2 is the forward reaction of hydrogen bromide formation, only with coefficients multiplied by 3/2. Therefore,

$$K_2 = K^{3/2} = (1.3 \times 10^{10})^{3/2} = \boxed{1.48 \times 10^{15}}$$

Lastly, reaction 3 is equivalent to reaction 2, only reversed. Thus,

$$K_3 = \frac{1}{K_2} = \frac{1}{1.48 \times 10^{15}} = \boxed{6.76 \times 10^{-16}}$$

◆ The correct answers are **1-A, 2-D** and **3-C**.

**Part 2:** Reaction 1 is simply the reverse reaction of the nitrogen-ammonia equilibrium, which means that

$$K_1 = \frac{1}{K} = \frac{1}{41} = \boxed{2.44 \times 10^{-2}}$$

Reaction 2, in turn, is the forward reaction of the nitrogen-ammonia equilibrium with halved stoichiometric coefficients, which is to say that

$$K_2 = K^{1/2} = 41^{1/2} = \boxed{6.40}$$

Lastly, reaction 3 is the forward reaction of the  $\text{N}_2\text{-NH}_3$  equilibrium with doubled coefficients, so that

$$K_3 = K^2 = 41^2 = \boxed{1.68 \times 10^3}$$

◆ The correct answers are **1-B, 2-B** and **3-C**.

**Part 3:** Reaction 3 is obtained by adding reactions 1 and 2. Accordingly,  $K_3 = K_1 \times K_2$ .

◆ The correct answer is **C**.

### P.7 → Solution

**Part 1:** To begin, we draw up the following concentration diagram.

Conc.	$\text{N}_2\text{O}_4$	$2\text{NO}$
Initial	1	0
Change	$-x$	$+2x$
Final	$1 - x$	$2x$

From the law of mass action, we have

$$K_p = \frac{(2x)^2}{1-x} \times (P/\Sigma n)^{\Delta n} = \frac{4x^2}{1-x} \times \left(\frac{180}{1+x}\right)^{2-1} = 680$$

$$\therefore \boxed{x = 0.697}$$

The equilibrium pressure for a dissociation of 80% is determined next,

$$K_p = \frac{4x^2}{1-x} \times \left(\frac{P}{1+x}\right)^1 = \frac{4 \times 0.8^2}{1-0.8} \times \left(\frac{P}{1+0.8}\right)^1 = 680$$

$$\therefore \boxed{P = 95.6 \text{ mmHg}}$$

◆ The correct answer is **B**.

**Part 2:** Since the molar mass of acetic acid is 60 g/mol, a mass of 120 g corresponds to  $120/60 = 2$  mol, and, since the cylinder has a volume of 1 L, the ensuing concentration is  $2/1 = 2$  M. Likewise, the number of moles of ethanol is  $92/46 = 2$  mol, and the concentration is  $2/1 = 2$  M. Equipped with this information, we draw up the following concentration diagram.

Conc.	AcH	Ethanol	Ester	Water
Initial	2	2	0	0
Change	-x	-x	+x	+x
Final	2 - x	2 - x	x	x

This brings to the following expression for the equilibrium constant.

$$K_c = \frac{[\text{Ester}][\text{H}_2\text{O}]}{[\text{AcH}][\text{Ethanol}]} = \frac{x \times x}{(2-x) \times (2-x)} = \frac{x^2}{(2-x)^2} = 4.0$$

Solving the quadratic equation above yields  $x = 1.33$ . It follows that the equilibrium mole fraction of ester is  $\chi_{\text{ester}} = 1.33/4 = 0.333$ .

◆ The correct answer is **B**.

**Part 3:** As usual, we begin by preparing a concentration diagram.

Conc.	N <sub>2</sub>	H <sub>2</sub>	NH <sub>3</sub>
Initial	1	3	0
Change	-x	-3x	+2x
Final	1 - x	3 - 3x	2x

Since the system pressure at equilibrium is 3 atm, the value of  $x$  easily follows,

$$(1-x) + (3-3x) + 2x = 3 \rightarrow x = 0.5 \text{ atm}$$

The partial pressures at equilibrium are determined next:

$$p(\text{N}_2) = \frac{1-x}{3} P = \frac{1-0.5}{3} \times 3 = 0.5 \text{ atm}$$

$$p(\text{H}_2) = \frac{3-3x}{3} \times 3 = \frac{3-3 \times 0.5}{3} \times 3 = 1.5 \text{ atm}$$

$$p(\text{NH}_3) = \frac{2x}{3} \times P = \frac{2 \times 0.5}{3} \times 3 = 1.0 \text{ atm}$$

Lastly, we can determine the equilibrium constant,

$$K_p = \frac{p(\text{NH}_3)^2}{p(\text{N}_2)p(\text{H}_2)^3} = \frac{1.0^2}{0.5 \times 1.5^3} = \boxed{0.593 \text{ atm}^{-2}}$$

◆ The correct answer is **C**.

**Part 4:** Consider the following concentration diagram.

Conc.	AB <sub>2</sub>	AB	B
Initial	500	0	0
Change	-x	+x	+x
Final	500 - x	x	x

We know that the equilibrium pressure is 600 torr. The value of  $x$  easily follows,

$$(500-x) + x + x = 600 \rightarrow x = 100 \text{ torr}$$

The equilibrium constant is determined next,

$$K_p = \frac{p(\text{AB})p(\text{B})}{p(\text{AB}_2)} = \frac{x \times x}{500-x} = \frac{100 \times 100}{500-100} = \boxed{25 \text{ torr}}$$

◆ The correct answer is **C**.

**Part 5:** To begin, we draw up the following concentration diagram.

Conc. (mol/L)	PCl <sub>5</sub>	PCl <sub>3</sub>	Cl <sub>2</sub>
Initial	1	0	0
Change	-x	+x	+x

Final	1 - x	x	x
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Appealing to the law of mass action yields

$$K = \frac{p(\text{PCl}_3)p(\text{Cl}_2)}{p(\text{PCl}_5)} \times (P/\Sigma n)^{\Delta n} = \frac{x \times x}{1-x} \times [P/(1+x)]^1$$

$$\therefore K = \frac{x^2}{1-x} \times \frac{P}{1+x} = \frac{Px^2}{1-x^2}$$

$$\therefore K = \frac{5 \times 0.15^2}{1-0.15^2} = 0.115 \text{ atm}$$

When  $x = 0.3$  and the temperature is unaltered,  $K$  should remain the same. Substituting  $x$  and solving for  $P$ , we obtain

$$K = \frac{Px^2}{1-x^2} \rightarrow P = \frac{K(1-x^2)}{x^2}$$

$$\therefore P = \frac{0.115 \times (1-0.3^2)}{0.3^2} = \boxed{1.16 \text{ atm}}$$

◆ The correct answer is **A**.

**Part 6:** To begin, we establish the equilibrium constant at 25°C,

$$K = \frac{p(\text{NO}_2)^2}{p(\text{N}_2\text{O}_4)} = \frac{0.4^2}{0.8} = 0.2 \text{ atm}$$

Then, we draw up the following concentration diagram.

Pres. (atm)	N <sub>2</sub> O <sub>4</sub>	NO <sub>2</sub>
Initial	1	0
Change	-x	2x
Final	1 - x	2x

Referring to the law of mass action, we have

$$K = \frac{n(\text{NO}_2)^2}{n(\text{N}_2\text{O}_4)} \times (P/\Sigma n)^{\Delta n} = \frac{(2x)^2}{(1-x)} \times \left(\frac{10}{1+x}\right)^1 = 0.2$$

Solving the quadratic equation above yields  $x = 0.0705$  atm. The partial pressures of the two gases easily follow,

$$p(\text{NO}_2) = \frac{2x}{1+x} P = \frac{2 \times 0.0705}{1+0.0705} \times 10 = \boxed{1.32 \text{ atm}}$$

$$p(\text{N}_2\text{O}_4) = \frac{1-x}{1+x} P = \frac{1-0.0705}{1+0.0705} \times 10 = \boxed{8.68 \text{ atm}}$$

◆ The correct answer is **D**.

**Part 7:** The equilibrium constant is

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{1.23^2}{0.5 \times 0.5} = 6.05$$

Once 0.6 mol of HI is removed, the concentrations become  $[\text{HI}] = 0.63 + 2x$  and  $[\text{H}_2] = [\text{I}_2] = 0.5 - x$ . From the law of mass action, we have

$$\frac{[\text{HI}]}{[\text{H}_2][\text{I}_2]} = \frac{(0.63 + 2x)^2}{(0.5 - x) \times (0.5 - x)} = 6.05$$

Solving the quadratic equation above yields  $x = 4.05$ , which is preposterous, and  $x = 0.134$ , which is a viable solution. The final concentrations of each compound are listed below.

Reactant/Product	Conc.
H <sub>2</sub>	0.366
I <sub>2</sub>	0.366
HI <sub>2</sub>	0.898

**Part 8:** Suppose  $x$  denotes the amount of  $O_2$  added to the mixture, and let  $y$  be the change in concentration after gaseous oxygen is added. We prepare the following concentration diagram.

Conc.	$SO_2$	$O_2$	$SO_3$
Initial	0.5	$0.12 + x$	5
Change	$-2y$	$-y$	$+2y$
Final	$0.5 - 2y$	$0.12 + x - y$	$5 + 2y$

Since  $5 + 2y = 5.2$ , we clearly have  $y = 0.1$ . Substituting in the law of mass action brings to

$$K_c = \frac{[SO_3]^2}{[SO_2]^2 [O_2]} = \frac{(5 + 2y)^2}{(0.5 - 2y)(0.12 + x - y)}$$

$$\therefore K_c = \frac{5.2^2}{0.3 \times (0.02 + x)} = 900$$

$$\therefore \boxed{x = 0.0801 \text{ mol}}$$

Approximately 0.08 mol of gaseous oxygen should be added to the system in order to increase the quantity of  $SO_3$  by the desired amount.

◆ The correct answer is **B**.

**Part 9:** To begin, we compute the equilibrium constant,

$$K = \frac{p(NO_2)^2}{p(N_2O_4)} = \frac{1.1^2}{0.28} = 4.32 \text{ atm}$$

If the container volume is doubled, the pressure will be halved and, by Le Chatelier's principle, the equilibrium will be shifted in the direction with more volume equivalents and, accordingly, the forward reaction will be favored. The new equilibrium pressure of  $NO_2$  will be  $1.1/2 + 2P$  and that of  $N_2O_4$  will be  $0.28/2 - P$ . Substituting in the law of mass action brings to

$$\frac{p(NO_2)^2}{p(N_2O_4)} = \frac{(1.1/2 + 2P)^2}{0.28/2 - P} = 4.32$$

Solving the quadratic equation above yields  $P = 0.0451$  atm. Thus, the partial pressures of  $N_2O_4$  and  $NO_2$  at the modified conditions are  $p(N_2O_4) = 0.28/2 - 0.0451 = 0.0949$  atm and  $p(NO_2) = 1.1/2 + 2 \times 0.0451 = 0.640$  atm. The results are summarized below.

Reactant/Product	Part. Pres. (atm)
$N_2O_4$	0.0949
$NO_2$	0.640

◆ The correct answer is **A**.

## P.8 → Solution

**Part 1:** A simple concentration diagram should yield the following partial pressures,

$$p(PCl_3) = \frac{\alpha}{1 + \alpha} P$$

$$p(Cl_2) = \frac{\alpha}{1 + \alpha} P$$

$$p(PCl_5) = \frac{1 - \alpha}{1 + \alpha} P$$

where  $\alpha = x/a$  is the degree of dissociation. Referring to the law of mass action, we have

$$K_p = \frac{p(PCl_3)p(Cl_2)}{p(PCl_5)} = \frac{\left(\frac{\alpha}{1 + \alpha}\right)P \times \left(\frac{\alpha}{1 + \alpha}\right)P}{\frac{1 - \alpha}{1 + \alpha}P}$$



$$\begin{aligned} \therefore K_p &= \frac{\alpha^2 P}{1 - \alpha^2} \\ \therefore K_p - K_p \alpha^2 &= \alpha^2 P \\ \therefore K_p &= \alpha^2 (P + K_p) \\ \therefore \frac{x}{a} &= \left( \frac{K_p}{P + K_p} \right)^{1/2} \end{aligned}$$

◆ The correct answer is **D**.

**Part 2:** As usual, the first step is to draw up a concentration diagram.

Conc.	H <sub>2</sub> O	H <sub>2</sub>	O <sub>2</sub>
Initial	1	0	0
Change	−α	+α	+α/2
Final	1 − α	α	α/2

The total number of moles is  $(1 - \alpha) + \alpha + \alpha = 1 + \alpha/2 = (2 + \alpha)/2$ . The partial pressures are, in turn,

$$p(\text{H}_2\text{O}) = \frac{1 - \alpha}{\left(\frac{2 + \alpha}{2}\right)} P = \frac{2(1 - \alpha)}{2 + \alpha} P$$

$$p(\text{H}_2) = \frac{\alpha}{\left(\frac{2 + \alpha}{2}\right)} P = \frac{2\alpha}{2 + \alpha} P$$

$$p(\text{O}_2) = \frac{\alpha/2}{\left(\frac{2 + \alpha}{2}\right)} P = \frac{\alpha}{2 + \alpha} P$$

Finally, we invoke the law of mass action to obtain

$$\begin{aligned} K_p &= \frac{p(\text{H}_2)p(\text{O}_2)^{1/2}}{p(\text{H}_2\text{O})} = \frac{\frac{2\alpha}{2 + \alpha} P \times \left(\frac{\alpha}{2 + \alpha} P\right)^{1/2}}{\frac{2(1 - \alpha)}{2 + \alpha} P} \\ \therefore K_p &= \frac{\cancel{2}\alpha}{\cancel{2 + \alpha}} \times \frac{\alpha^{1/2}}{(2 + \alpha)^{1/2}} P^{1/2} \times \frac{\cancel{2 + \alpha}}{\cancel{2}(1 - \alpha)} \frac{1}{\cancel{P}} \\ \therefore K_p &= \frac{\alpha^{3/2} P^{1/2}}{(1 - \alpha)(2 + \alpha)^{1/2}} \end{aligned}$$

◆ The correct answer is **C**.

## P.9 → Solution

**Part 1:** Increasing pressure shifts the equilibrium in favor of the reaction that reduces the number of volume-equivalents of gas. In equilibria P, R and S, the number of moles of gas is the same in either side of the reaction, which implies that a raise in pressure would not displace the equilibrium at all. However, in reaction Q the number of moles of gas in the products side (1 volume-equivalent of CO<sub>2</sub>) is different from that in the reactants side (zero volume-equivalents of gas), so that an augmented pressure would favor the back reaction.

◆ The correct answer is **D**.

**Part 2:** Increasing the amount of hydrogen, a reactant, would displace the equilibrium towards the formation of products. Reducing the temperature would favor the exothermic reaction, which in the present case happens to be the forward reaction. Increasing pressure would favor the reaction that decreases the number of volume equivalents of gas, which in the case at hand happens to be the forward reaction. Lastly, adding argon, an inert gas, to the system would not affect the partial pressures of the gases and hence wouldn't affect equilibrium at all.

◆ The correct answer is **B**.

**Part 3:** Increasing the temperature favors the endothermic reaction – namely, the formation of ozone. In turn, increasing the pressure favors the reaction that lowers the number of volume-equivalents of gas – again, the formation of ozone. Production of ozone is favored by increasing temperature and pressure.

◆ The correct answer is **A**.

**Part 4:** Adjustment P, reducing the volume – or, equivalently, increasing pressure – favors the reaction that reduces the number of volume-equivalents of gas, which, in the present case, happens to be the back reaction. Adjustment Q, adding more  $\text{NO}_2$ , also favors the back reaction. Adjustment R, adding more  $\text{N}_2\text{O}_4$ , will displace the equilibrium toward the formation of products, that is, it enhances the forward reaction. Adding an inert gas such as argon does not affect the partial pressures of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  and hence does not displace the equilibrium at all.

◆ The correct answer is **B**.

**Part 5:** Increasing temperature favors the endothermic reaction, or, in the present case, the formation of CO. Reducing pressure favors the reaction that increases the number of volume-equivalents of gas, or, in the system at hand, the formation of CO. Adding solid carbon, a solid reactant, does not alter the equilibrium at all. Likewise, adding a catalyst generally increases reaction speed and reduces activation energy but leaves equilibrium unchanged.

◆ The correct answer is **B**.

### P.10 → Solution

**Part 1:** With reference to the data in Table 2, the reaction enthalpy for the decomposition of  $\text{N}_2\text{O}_4$  is

$$\begin{aligned}\Delta H_r^\circ &= 2\Delta H_f^\circ[\text{NO}_2] - \Delta H_f^\circ[\text{N}_2\text{O}_4] \\ \therefore \Delta H_r^\circ &= 2 \times 33.2 - 9.16 = 57.2 \text{ kJ/mol}\end{aligned}$$

The equilibrium constant follows from the van't Hoff equation,

$$\begin{aligned}\ln \frac{K_2}{K_1} &= \frac{\Delta H_r^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \rightarrow \ln \left( \frac{K_2}{0.15} \right) = \frac{57,200}{8.314} \times \left( \frac{1}{298} - \frac{1}{500} \right) \\ \therefore K_2 &= 1.69 \times 10^3\end{aligned}$$

◆ The correct answer is **C**.

**Part 2:** With reference to the data in Table 2, the reaction enthalpy for decomposition of  $\text{PCl}_5$  is

$$\begin{aligned}\Delta H_r^\circ &= \Delta H_f^\circ[\text{PCl}_3] + \Delta H_f^\circ[\text{Cl}_2] - \Delta H_f^\circ[\text{PCl}_5] \\ \therefore \Delta H_r^\circ &= -287.0 + 0 - (-374.9) = 87.9 \text{ kJ/mol}\end{aligned}$$

The equilibrium constant follows from the van't Hoff equation,

$$\begin{aligned}\ln \frac{K_2}{K_1} &= \frac{\Delta H_r^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \rightarrow \ln \left( \frac{K_2}{78.3} \right) = \frac{87,900}{8.314} \times \left( \frac{1}{523} - \frac{1}{800} \right) \\ \therefore K_2 &= 8.58 \times 10^4\end{aligned}$$

◆ The correct answer is **C**.

**Part 3:** With reference to the data in Table 2, the reaction enthalpy for decomposition of  $\text{SO}_3$  is

$$\begin{aligned}\Delta H_r^\circ &= 2\Delta H_f^\circ[\text{SO}_2] + \Delta H_f^\circ[\text{O}_2] - 2\Delta H_f^\circ[\text{SO}_3] \\ \therefore \Delta H_r^\circ &= 2 \times (-296.8) + 0 - 2 \times (-395.7) = 197.8 \text{ kJ/mol}\end{aligned}$$

Then, the equilibrium constant can be obtained by dint of the van't Hoff equation,

$$\begin{aligned}\ln \frac{K_2}{K_1} &= \frac{\Delta H_r^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \rightarrow \ln \left( \frac{K_2}{2.5 \times 10^{-25}} \right) = \frac{197,800}{8.314} \times \left( \frac{1}{298} - \frac{1}{500} \right) \\ \therefore K_2 &= 2.54 \times 10^{-11}\end{aligned}$$

◆ The correct answer is **A**.

## ▶ ANSWER SUMMARY

Problem 1		A
Problem 2		Open-ended pb.
Problem 3	3.1	$\beta$
	3.2	$\alpha$
	3.3	$\alpha$
Problem 4	4.1	D
	4.2	C
	4.3	B
	4.4	D
	4.5	A
	4.6	A
	4.7	C
Problem 5	5.1	D
	5.2	B
	5.3	A
Problem 6	6.1	1-A, 2-D, 3-C
	6.2	1-B, 2-B, 3-C
	6.3	C
Problem 7	7.1	B
	7.2	B
	7.3	C
	7.4	C
	7.5	A
	7.6	D
	7.7	Open-ended pb.
	7.8	B
	7.9	A
Problem 8	8.1	D
	8.2	C
Problem 9	9.1	D
	9.2	B
	9.3	A
	9.4	B
	9.5	B
Problem 10	10.1	C
	10.2	C
	10.3	A

## ▶ REFERENCES

- AGARWAL, O. and YADAV, J. (2010). *Disha's IIT-JEE Chemistry Challenger*. New Delhi: Disha.
- ATKINS, P. and JONES, L. (2010). *Chemical Principles*. 5th edition. New York: W.H. Freeman and Company.
- GANGULY, A. (2012). *Fundamentals of Physical Chemistry for Competitive Examinations*. 2nd edition. Upper Saddle River: Pearson.
- SINGHAL, A. (2010). *The Pearson Guide to Physical Chemistry for the IIT-JEE*. Upper Saddle River: Pearson.



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