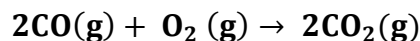


Constant: $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

- 1. (10%) What is K_p at 1273°C for the reaction**



if K_c is 2.24×10^{-22} at the same temperature?

Sol.

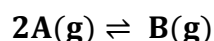
Using Equation 10.6 of the text: $K_p = K_c (0.08314 T)^{\Delta n}$

where, $\Delta n = 2 - 3 = -1$

and $T = (1273 + 273) \text{ K} = 1546 \text{ K}$

$$K_p = (2.24 \times 10^{-22})(0.08314 \times 1546)^{-1} = \mathbf{1.74 \times 10^{-24}}$$

- 2. (10%) At a certain temperature and a total pressure of 1.2 bar, the partial pressures of an equilibrium mixture**



are $P_A = 0.60 \text{ bar}$ and $P_B = 0.60 \text{ bar}$. (a) Calculate the K_p for the reaction at this temperature. (b) If the total pressure were increased to 1.5 bar, what would be the partial pressures of A and B at equilibrium?

Sol.

(a) Calculate the value of K_p by substituting the equilibrium partial pressures into the equilibrium constant expression.

$$K_p = \frac{P_B}{P_A^2} = \frac{(0.60)}{(0.60)^2} = \mathbf{1.7}$$

(b) The total pressure is the sum of the partial pressures for the two gaseous components, A and B. We can write:

$$P_A + P_B = 1.5 \text{ bar}$$

$$P_B = 1.5 - P_A$$

Substituting into the expression for K_p gives:

$$K_p = \frac{(1.5 - P_A)}{P_A^2} = 1.7$$

$$1.7P_A^2 + P_A - 1.5 = 0$$

Solving the quadratic equation, we obtain:

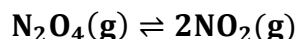
$$P_A = \mathbf{0.69 \text{ bar}}$$

$$P_B = \mathbf{0.81 \text{ bar}}$$

Check that substituting these equilibrium concentrations into the equilibrium constant expression gives the equilibrium constant calculated in part (a).

$$K_P = \frac{P_B}{P_A^2} = \frac{0.81}{(0.69)^2} = 1.7$$

3. (10%) Consider the reaction between NO_2 and N_2O_4 in a closed container:



Initially there is 1 mole of N_2O_4 present. At equilibrium, α mole of N_2O_4 has dissociated to form NO_2 . (a) Derive an expression for K_P in terms of α and P , the total pressure. (b) How does the expression in part (a) help you predict the shift in the equilibrium concentrations due to an increase in P ? Does your prediction agree with Le Chatelier's principle?

Sol.

(a) The total number of moles present in the system $= (1 - \alpha) + 2\alpha = 1 + \alpha$. The partial pressure is equal to the mole fraction times the total pressure (P_{total}).

$$P_{\text{N}_2\text{O}_4} = X_{\text{N}_2\text{O}_4} P_{\text{total}} = \frac{1 - \alpha}{1 + \alpha} P_{\text{total}}$$

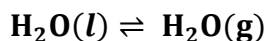
$$P_{\text{NO}_2} = X_{\text{NO}_2} P_{\text{total}} = \frac{2\alpha}{1 + \alpha} P_{\text{total}}$$

We can now plug these expressions in to the expression for the equilibrium constant.

$$K_P = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} = \left(\frac{2\alpha P_{\text{total}}}{1 + \alpha} \right)^2 \left(\frac{1 + \alpha}{(1 - \alpha) P_{\text{total}}} \right) = \frac{4\alpha^2 P_{\text{total}}}{(1 + \alpha)(1 - \alpha)} = \frac{4\alpha^2 P_{\text{total}}}{1 - \alpha^2}$$

(b) Because the equilibrium constant is independent of pressure, as P_{total} increases, α decreases to keep the right side of the above equation constant. This is consistent with Le Châtelier's principle.

4. (10%) At 25°C , ΔG_{rxn} for the process



is 8.6 kJ mol^{-1} . Calculate the vapor pressure of water at this temperature.

Sol.

The equilibrium constant expression is:

$$K_P \approx P_{\text{H}_2\text{O}}$$

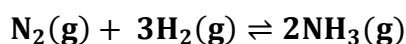
We are actually finding the equilibrium vapor pressure of water. We use

Equation 10.12 of the text.

$$P_{\text{H}_2\text{O}} = K_P = e^{\frac{-\Delta G^\circ}{RT}} = e^{\frac{-8.6 \times 10^3 \text{ J mol}^{-1}}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}} = e^{-3.47} = 3.1 \times 10^{-2} \text{ bar}$$

The positive value of ΔG° implies that reactants are favored at equilibrium at 25°C. Is that what you would expect?

5. (10%) The equilibrium constant K_P for the following reaction is 4.26×10^{-4} at 375°C:



In a certain experiment, a student starts with 0.884 bar of N_2 and 0.383 bar of H_2 in a constant-volume vessel at 375°C. Calculate the partial pressures of all species when equilibrium is reached.

Sol.

According to the ideal gas law, pressure is directly proportional to the concentration of a gas in mol L^{-1} if the reaction is at constant volume and temperature. Therefore, pressure may be used as a concentration unit. The reaction is:

	N_2	+	3H_2	\longrightarrow	2NH_3
Initial (bar):	0.884		0.383		0
Change (bar):	$-x$		$-3x$		$+2x$
Equilibrium (bar):	$(0.884 - x)$		$(0.383 - 3x)$		$2x$

$$K_P \approx \frac{P_{\text{NH}_3}^2}{P_{\text{H}_2}^3 P_{\text{N}_2}}$$

$$4.26 \times 10^{-4} = \frac{(2x)^2}{(0.383 - 3x)^3 (0.884 - x)}$$

At this point, we can make two assumptions that $3x$ is very small compared to 0.383 and that x is very small compared to 0.884. Hence,

$$0.383 - 3x \approx 0.383$$

$$0.884 - x \approx 0.884$$

$$4.31 \times 10^{-4} \approx \frac{(2x)^2}{(0.383)^3 (0.884)}$$

Solving for x .

$$x = 2.31 \times 10^{-3} \text{ bar}$$

The equilibrium pressures are:

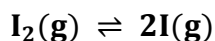
$$P_{\text{N}_2} = [0.884 - (2.31 \times 10^{-3})] \text{ bar} = \mathbf{0.882 \text{ bar}}$$

$$P_{\text{H}_2} = [0.373 - (3)(2.31 \times 10^{-3})] \text{ bar} = \mathbf{0.366 \text{ bar}}$$

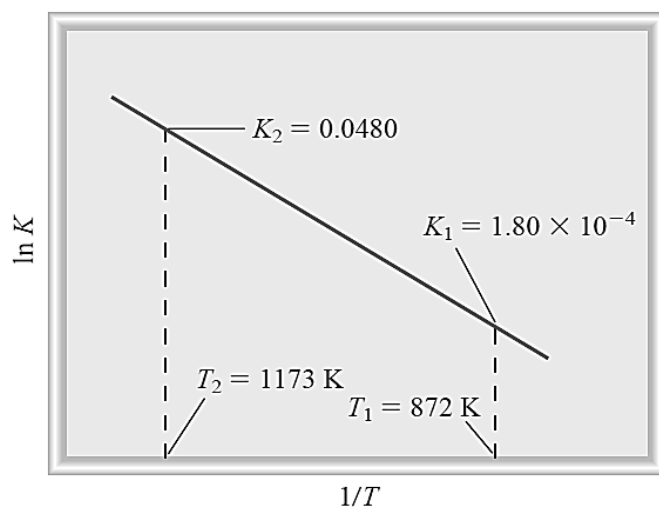
$$P_{\text{NH}_3} = (2)(2.31 \times 10^{-3} \text{ bar}) = \mathbf{4.63 \times 10^{-3} \text{ bar}}$$

Was the assumption valid that we made above? Typically, the assumption is considered valid if x is less than 5 percent of the number that we said it was very small compared to. Is this the case?

6. (10%) The following diagram shows the variation of the equilibrium constant with temperature for the reaction



Calculate ΔG° , ΔH° , and ΔS° for the reaction at 872 K.



Sol.

We can calculate ΔG° at 872 K from the equilibrium constant, K_1 .

$$\Delta G^\circ = -RT \ln K$$

$$\Delta G^\circ = -(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(872 \text{ K}) \ln(1.80 \times 10^{-4})$$

$$\Delta G^\circ = 6.25 \times 10^4 \text{ J mol}^{-1} = \mathbf{62.5 \text{ kJ mol}^{-1}}$$

We can use Equation 10.16 in the text to calculate ΔH° .

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{0.0480}{1.80 \times 10^{-4}} = \frac{\Delta H^\circ}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \left(\frac{1}{872 \text{ K}} - \frac{1}{1173 \text{ K}} \right)$$

$$\Delta H^\circ = 157.8 \text{ kJ mol}^{-1}$$

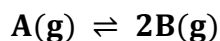
Now that both ΔG° and ΔH° are known, we can calculate ΔS° at 872 K.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$62.5 \times 10^3 \text{ J mol}^{-1} = (157.8 \times 10^3 \text{ J mol}^{-1}) - (872 \text{ K})\Delta S^\circ$$

$$\Delta S^\circ = 109 \text{ J mol}^{-1} \text{ K}^{-1}$$

7. (10%) Consider the following reaction at equilibrium:



From the following data, calculate the equilibrium constant (both K_P and K_c) at each temperature. Is the reaction endothermic or exothermic?

Temperature (°C)	[A] (M)	[B] (M)
200	0.0125	0.843
300	0.171	0.764
400	0.250	0.724

Sol.

The relevant relationships are:

$$K_c \approx \frac{[\text{B}]^2}{[\text{A}]} \quad \text{and} \quad K_P = \frac{P_B^2}{P_A}$$

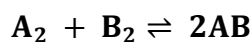
$$K_P = K_c (0.08314 T)^{\Delta n} = K_c (0.08314 T) \Delta n = +1$$

We set up a table for the calculated values of K_c and K_P .

T (°C)	K_c	K_P
200	$\frac{(0.843)^2}{(0.0125)} = 56.9$	$56.9(0.08314 \times 473) = 2.24 \times 10^3$
300	$\frac{(0.764)^2}{(0.171)} = 3.41$	$3.41(0.08314 \times 573) = 1.62 \times 10^2$
400	$\frac{(0.724)^2}{(0.250)} = 2.10$	$2.10(0.08314 \times 673) = 118$

Since K_c (and K_P) decrease with temperature, the reaction is exothermic.

8. (10%) Consider the following reaction at a certain temperature:



The mixing of 1 mole of A_2 with 3 moles of B_2 gives rise to x moles of AB at equilibrium. The addition of 2 more moles of A_2 produces another x moles of AB.

What is the equilibrium constant for the reaction?

Sol.

We start with a table.

	A_2	+	B_2	\rightarrow	2AB
Initial (mol):	1		3		0
Change (mol):	$-\frac{x}{2}$		$-\frac{x}{2}$		$+x$
<hr/>					
Equilibrium (mol):	$1 - \frac{x}{2}$		$3 - \frac{x}{2}$		x

After the addition of 2 moles of A,

	A_2	+	B_2	\rightarrow	2AB
Initial (mol):	$3 - \frac{x}{2}$		$3 - \frac{x}{2}$		x
Change (mol):	$-\frac{x}{2}$		$-\frac{x}{2}$		$+x$
<hr/>					
Equilibrium (mol):	$3 - x$		$3 - x$		$2x$

We write two different equilibrium constants expressions for the two tables.

$$K \approx \frac{[\text{AB}]^2}{[\text{A}_2][\text{B}_2]}$$

$$K \approx \frac{x^2}{\left(1 - \frac{x}{2}\right)\left(3 - \frac{x}{2}\right)} \quad \text{and} \quad K = \frac{(2x)^2}{(3-x)(3-x)}$$

We equate the equilibrium constant expressions and solve for x .

$$\frac{x^2}{\left(1 - \frac{x}{2}\right)\left(3 - \frac{x}{2}\right)} = \frac{(2x)^2}{(3-x)(3-x)}$$

$$\frac{1}{\frac{1}{4}(x^2 - 8x + 12)} = \frac{4}{x^2 - 6x + 9}$$

$$-6x + 9 = -8x + 12$$

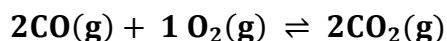
$$x = 1.5$$

We substitute x back into one of the equilibrium constant expressions to solve for K .

$$K \approx \frac{(2x)^2}{(3-x)(3-x)} = \frac{(3)^2}{(1.5)(1.5)} = 4.0$$

Substitute x into the other equilibrium constant expression to see if you obtain the same value for K . Note that we used moles rather than molarity for the concentrations, because the volume, V , cancels in the equilibrium constant expressions.

9. (10%) Consider the gas-phase reaction



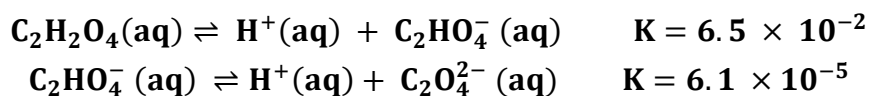
Predict the shift in the equilibrium position when helium gas is added to the equilibrium mixture (a) at constant pressure and (b) at constant volume.

Sol.

(a) If helium gas is added to the system without changing the pressure or the temperature, the volume of the container must necessarily be increased. This will decrease the partial pressures of all the reactants and products. A pressure decrease will favor the reaction that increases the number of moles of gas. The position of equilibrium will shift to the **left**.

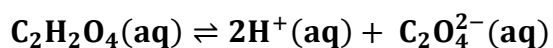
(b) If the volume remains unchanged, the partial pressures of all the reactants and products will remain the same. The reaction quotient Q_c will still equal the equilibrium constant, and there will be **no change** in the position of equilibrium.

10. (10%) The following equilibrium constants have been determined for oxalic acid at 25°C:



Calculate the equilibrium constant for the following reaction at the same

temperature:



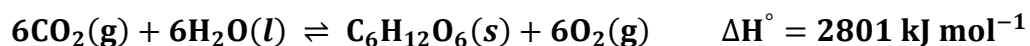
Sol.

$$K = K' K''$$

$$K = (6.5 \times 10^{-2}) (6.1 \times 10^{-5})$$

$$K = 4.0 \times 10^{-6}$$

11. (10%) Photosynthesis can be represented by



Explain how the equilibrium would be affected by the following changes: (a) partial pressure of CO_2 is increased, (b) O_2 is removed from the mixture, (c) $\text{C}_6\text{H}_{12}\text{O}_6$ (glucose) is removed from the mixture, (d) more water is added, or (e) temperature is decreased.

Sol.

- (a)** shifts to right
- (b)** shifts to right
- (c)** no change
- (d)** no change
- (e)** shifts to left