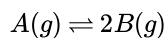


## 7.5: Degree of Dissociation

Reactions such as the one in the previous example involve the dissociation of a molecule. Such reactions can be easily described in terms of the fraction of reactant molecules that actually dissociate to achieve equilibrium in a sample. This fraction is called the **degree of dissociation**. For the reaction in the previous example



the degree of dissociation can be used to fill out an ICE table. If the reaction is started with  $n$  moles of  $A$ , and  $\alpha$  is the fraction of  $A$  molecules that dissociate, the ICE table will look as follows.

	$A$	$2B$
<b>Initial</b>	$n$	0
<b>Change</b>	$-\alpha n$	$+2n\alpha$
<b>Equilibrium</b>	$n(1 - \alpha)$	$2n\alpha$

The mole fractions of  $A$  and  $B$  can then be expressed by

$$\begin{aligned}\chi_A &= \frac{n(1 - \alpha)}{n(1 - \alpha) + 2n\alpha} \\ &= \frac{1 - \alpha}{1 + \alpha} \\ \chi_B &= \frac{2\alpha}{1 + \alpha}\end{aligned}$$

Based on these mole fractions

$$K_x = \frac{\left(\frac{2\alpha}{1 + \alpha}\right)^2}{\frac{1 - \alpha}{1 + \alpha}} \quad (7.5.1)$$

$$= \frac{4\alpha^2}{1 - \alpha^2} \quad (7.5.2)$$

And so  $K_p$ , which can be expressed as

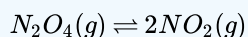
$$K_p = K_x (p_{tot})^{\sum \nu_i} \quad (7.5.3)$$

is given by

$$K_p = \frac{4\alpha^2}{(1 - \alpha^2)} (p_{tot})$$

### ✓ Example 7.5.1

Based on the values given below, find the equilibrium constant at 25 °C and degree of dissociation for a system that is at a total pressure of 1.00 atm for the reaction



	$N_2O_4(g)$	$NO_2(g)$
$\Delta G_f^\circ$ (kJ/mol)	99.8	51.3

### Solution

First, the value of  $K_p$  can be determined from  $\Delta G_{rxn}^\circ$  via an application of Hess' Law.

$$\Delta G_{rxn}^{\circ} = 2 (51.3 \text{ kJ/mol}) - 99.8 \text{ kJ/mol} = 2.8 \text{ kJ/mol}$$

So, using the relationship between thermodynamics and equilibria

$$\Delta G_f^{\circ} = -RT \ln K_p$$

$$2800 \text{ kJ/mol} = -(8.314 \text{ J/(mol K)})(298 \text{ K}) \ln K_p$$

$$K_p = 0.323 \text{ atm}$$

The degree of dissociation can then be calculated from the ICE tables at the top of the page for the dissociation of  $N_2O_4(g)$ :

$$K_p = \frac{4\alpha^2}{1 - \alpha^2} (p_{tot})$$

$$0.323 \text{ atm} = \frac{4\alpha^2}{1 - \alpha^2} (1.00 \text{ atm})$$

Solving for  $\alpha$ ,

$$\alpha = 0.273$$

*Note:* since  $\alpha$  represents the fraction of  $N_2O_4$  molecules dissociated, it **must** be a positive number between 0 and 1.

### ✓ Example 7.5.2

Consider the gas-phase reaction



A reaction vessel is initially filled with 1.00 mol of A and 2.00 mol of B. At equilibrium, the vessel contains 0.60 mol C and a total pressure of 0.890 atm at 1350 K.

1. How many mol of A and B are present at equilibrium?
2. What is the mole fraction of A, B, and C at equilibrium?
3. Find values for  $K_x$ ,  $K_p$ , and  $\Delta G_{rxn}^{\circ}$ .

#### Solution

Let's build an ICE table!

	A	2 B	2 C
<b>Initial</b>	1.00 mol	2.00 mol	0
<b>Change</b>	-x	-2x	+2x
<b>Equilibrium</b>	1.00 mol - x	2.00 mol - 2x	2x = 0.60 mol

From the equilibrium measurement of the number of moles of C,  $x = 0.30$  mol. So at equilibrium,

	A	2 B	2 C
<b>Equilibrium</b>	0.70 mol	1.40 mol	0.60 mol

The total number of moles at equilibrium is 2.70 mol. From these data, the mole fractions can be determined.

$$\chi_A = \frac{0.70 \text{ mol}}{2.70 \text{ mol}} = 0.259$$

$$\chi_B = \frac{1.40 \text{ mol}}{2.70 \text{ mol}} = 0.519$$

$$\chi_C = \frac{0.60 \text{ mol}}{2.70 \text{ mol}} = 0.222$$

So  $K_x$  is given by

$$K_x = \frac{(0.222)^2}{(0.259)(0.519)^2} = 0.7064$$

And  $K_p$  is given by Equation 7.5.3, so

$$K_p = 0.7604(0.890 \text{ atm})^{-1} = 0.792 \text{ atm}^{-1}$$

The thermodynamic equilibrium constant is unitless, of course, since the pressures are all divided by 1 atm. So the actual value of  $K_p$  is 0.794. This value can be used to calculate  $\Delta G_{rxn}^o$  using

$$\Delta G_{rxn}^o = -RT \ln K_p$$

so

$$\begin{aligned}\Delta G_{rxn}^o &= -(8.314 \text{ J/(mol K)})(1350 \text{ K}) \ln(0.792) \\ &= 2590 \text{ J/mol}\end{aligned}$$

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