❖ Law of Mass Action and Its Thermodynamic Derivation

According to the law of mass action, the rate of a chemical reaction is directly proportional to the product of the activities or simply the active masses of the reactants each term raised to its stoichiometric coefficients.

To understand the law of mass action in mathematical language, consider a reaction in which two reactants *A* and *B* react to form the product *C* and *D* i.e.

$$aA + bB \rightarrow cC + dD \tag{33}$$

Then the law of mass action says the rate of the above conversion should be

$$Rate \propto [A]^a[B]^b \tag{34}$$

$$Rate = k[A]^a[B]^b \tag{35}$$

Where *k* is the constant of proportionality and is typically labeled as rate constant of the reaction.

However, the actual rate of the reaction may or may not be equal to what is suggested by the "law of mass action" because the actual rate law may have powers raised to the active masses different from their stoichiometric coefficients. Mathematically, the actual rate law for the reaction given by equation (33) is

$$Rate \propto [A]^\alpha[B]^\beta \tag{36}$$

$$Rate = k[A]^\alpha[B]^\beta \tag{37}$$

Now comparing equation (35) and equation (37); the law of mass action and actual rate law will give same results when $a = \alpha$ and $b = \beta$; whereas different results will be observed when $a \neq \alpha$ and $b \neq \beta$.

➢ *Modern Definition of the Law of Mass Action*

The law of mass action can be used to study the composition of a mixture in a reversible reaction under equilibrium conditions. To do so, consider a typical reversible reaction i.e.

$$aA + bB \rightleftharpoons cC + dD \tag{38}$$

Now, from the law of mass action, we know that the rate of forward reaction (R_f) and rate backward reaction (R_b) will be

$$R_f = k_f[A]^a[B]^b \tag{39}$$

$$R_b = k_b[C]^c[D]^d \tag{40}$$

Where k_f and k_b are the rate constants for the forward and backward reactions, respectively. After equilibrium is reached, we have

$$R_f = R_b \tag{41}$$

$$k_f[A]^a[B]^b = k_b[C]^c[D]^d \tag{42}$$

or

$$\frac{k_f}{k_b} = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{43}$$

Since the k_f and k_b are also constant at equilibrium, the ratio of the two is also a constant and is typically labeled as K or the equilibrium constant. Therefore, equation (43) is modified as

$$K = \frac{k_f}{k_b} = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{44}$$

All this leads to the modern definition of "law of mass action" that the ratio of the multiplication of molar concentrations of products raised to the power of their stoichiometric coefficients to the multiplication of the molar concentrations of the reactants raised to the power of their stoichiometric coefficients is constant at constant temperature and is called as "equilibrium constant". It is also worthy to mention that equation (44) is also known as the "law of chemical equilibrium".

- ***Thermodynamic Derivation of the Law of Mass Action***

In order to derive the law of mass action thermodynamically, recall the general form of a typical reversible reaction under equilibrium conditions in which reactants and products are ideal gases i.e.

$$aA + bB \rightleftharpoons cC + dD \tag{45}$$

Now, as we know that the total free energy of the reactant (G_R) can be formulated as

$$G_R = a\mu_A + b\mu_B \tag{46}$$

Where μ_A and μ_B are the chemical potentials of reactant A and B, respectively. Similarly, the total free energy of the products (G_P) can also be formulated i.e.

$$G_P = c\mu_C + d\mu_D \tag{47}$$

It is also important to mention that the temperature and pressure are kept constant. Moreover, the free energy change of the whole reaction can be obtained by subtracting equation (46) from equation (47) i.e.

$$\Delta G_{reaction} = G_P - G_R \tag{48}$$

$$\Delta G_{reaction} = (c\mu_C + d\mu_D) - (a\mu_A + b\mu_B) \tag{49}$$

Recalling the fact that the free energy change at equilibrium is zero, equation (49) is reduced to

$$(c\mu_C + d\mu_D) - (a\mu_A + b\mu_B) = 0 \tag{51}$$

Now recall the expression of the chemical potential of the ith species in gas phase i.e.

$$\mu_i = \mu_i^0 + RT\ln p_i \tag{52}$$

Where p_i and μ_i^0 are the partial pressure and standard chemical potential of ith species, respectively. Now using equation (52) in equation (51), we get

$$[c(\mu_C^0 + RT\ln p_C) + d(\mu_D^0 + RT\ln p_D)] - [a(\mu_A^0 + RT\ln p_A) + b(\mu_B^0 + RT\ln p_B)] = 0 \tag{53}$$

or

$$c\mu_C^0 + cRT\ln p_C + d\mu_D^0 + dRT\ln p_D - a\mu_A^0 - aRT\ln p_A - b\mu_B^0 - bRT\ln p_B = 0 \tag{54}$$

$$c\mu_C^0 + RT\ln p_C^c + d\mu_D^0 + RT\ln p_D^d - a\mu_A^0 - RT\ln p_A^a - b\mu_B^0 - RT\ln p_B^b = 0 \tag{55}$$

$$RT\ln p_C^c + RT\ln p_D^d - RT\ln p_A^a - RT\ln p_B^b = -c\mu_C^0 - d\mu_D^0 + a\mu_A^0 + b\mu_B^0$$

or

$$RT\ln\left(p_C^c p_D^d\right) - RT\ln\left(p_A^a p_B^b\right) = -[c\mu_C^0 + d\mu_D^0 - a\mu_A^0 - b\mu_B^0] \tag{56}$$

$$RT\ln\frac{\left(p_C^c p_D^d\right)}{\left(p_A^a p_B^b\right)} = -[G_P^o - G_R^o] \tag{57}$$

$$RT\ln\frac{\left(p_C^c p_D^d\right)}{\left(p_A^a p_B^b\right)} = -\Delta G_{reaction}^o \tag{58}$$

Where $\Delta G_{reaction}^o$ is the standard free energy change of the reaction can be simply abbreviated as ΔG^o only. Therefore, the equation (58) can be rearranged as given below.

$$\ln\frac{\left(p_C^c p_D^d\right)}{\left(p_A^a p_B^b\right)} = -\frac{\Delta G^o}{RT} \tag{59}$$

$$\frac{p_C^c p_D^d}{p_A^a p_B^b} = e^{-\frac{\Delta G^o}{RT}} \tag{61}$$

Now because ΔG^o is a function of temperature only and R is a constant quantity, the right-hand side can be put equal to another constant, say 'K_p'.

$$e^{-\frac{\Delta G^o}{RT}} = K_p \tag{62}$$

From equation (61) and equation (62), we have

$$K_p = \frac{p_C^c p_D^d}{p_A^a p_B^b} \tag{63}$$

Which is again the modern statement of "law of mass action" but in terms of partial pressures.

Other forms of equation (63) can also be written depending upon the reactants and products involved. If the chemical potentials of the reactants and products are in mole fractions (x_i) i.e.

$$\mu_i = \mu_i^0 + RT \ln x_i \tag{64}$$

Then equation (63) takes the form

$$K_x = \frac{x_C^c \, x_D^d}{x_A^a \, x_B^b} \tag{65}$$

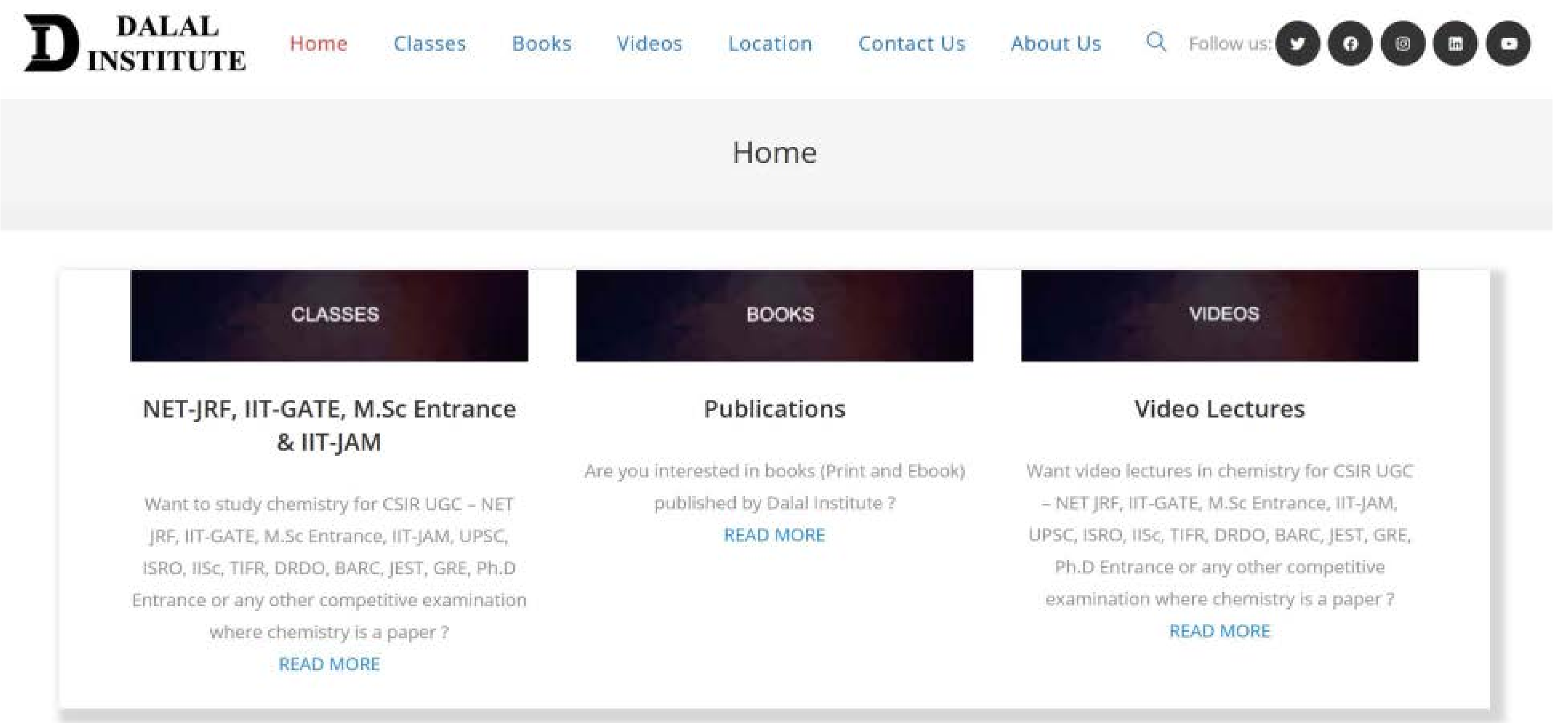
Similarly, If the chemical potentials of the reactants and products are in molar concentrations (c_i) i.e.

$$\mu_i = \mu_i^0 + RT \ln c_i \tag{66}$$

Then equation (63) takes the form

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{67}$$

Which is the popular form of "law of mass action".



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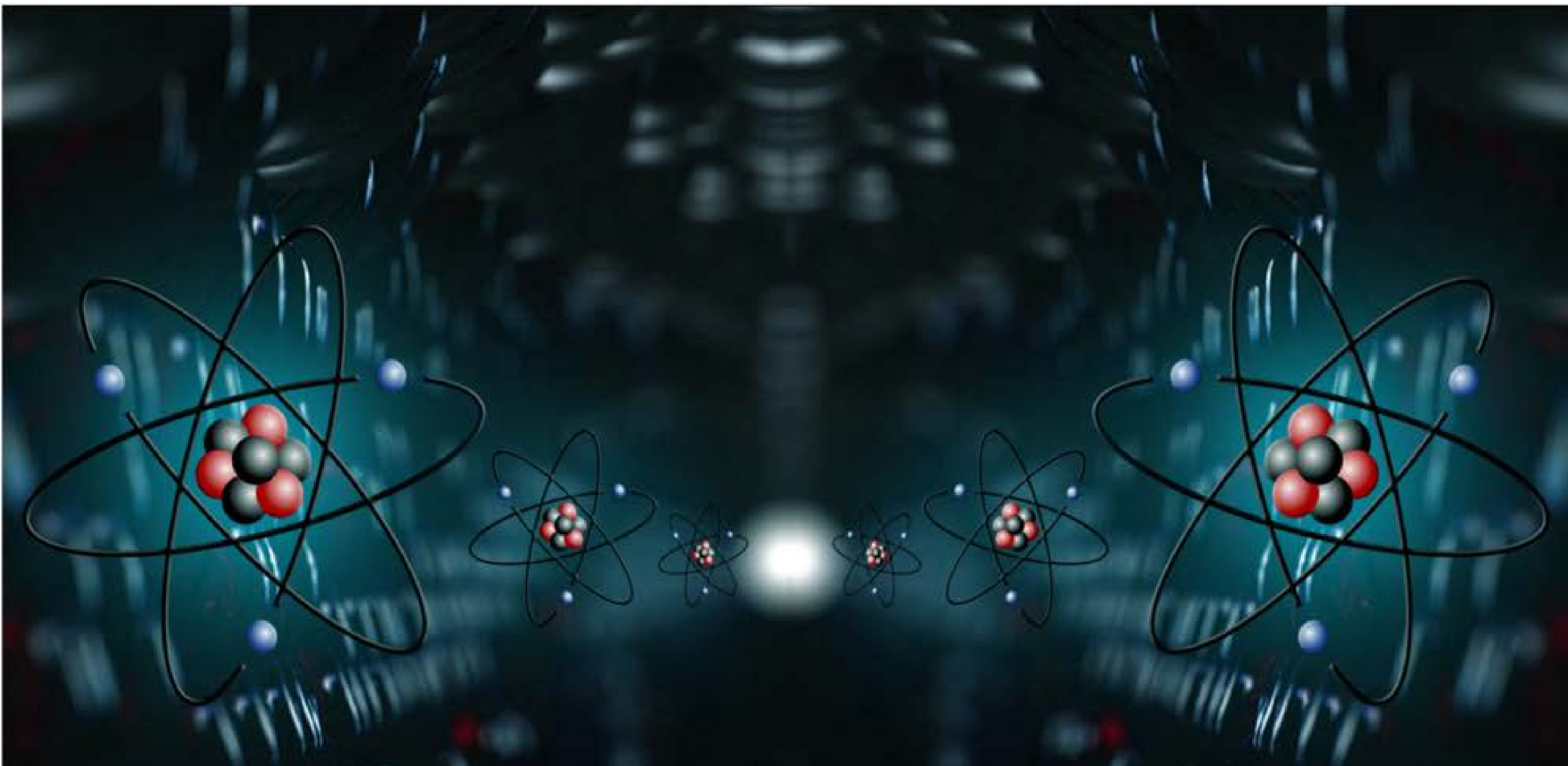

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