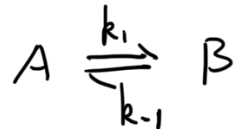


5_Verification of Onsager Relations_Irreversible Thermodynamics

Link: https://www.youtube.com/watch?v=PAWX0WUoHWg&list=PLdBDmcnzLC_ZMUWMdy7SmcTgnnzyiRpql&index=5

In both kinetic & Thermodynamic way.



$$-\frac{dC_A}{dt} = k_1 C_A - k_{-1} C_B$$

$$\frac{dC_B}{dt} = k_1 C_A - k_{-1} C_B$$

Local Equilibrium Postulate:

In irreversible Thermodynamics, we are considering that our system is divided into large numbers of very small systems and these small systems are under their own equilibrium.

$$\textcircled{a} \text{ Equilibrium, } J_{ch} = -\frac{dC_A}{dt} = \frac{dC_B}{dt} = 0$$

↑
Macroscopic
chemical reaction rate

Hence, we can write

$$k_1 C_A^e = k_{-1} C_B^e \quad \rightarrow \text{refers to equilibrium condition}$$

↓

Equilibrium
Constant
ratio $\rightarrow K = \frac{k_1}{k_{-1}} = \frac{C_B^e}{C_A^e}$

If α is the extent to which the reaction has reacted.

$$\alpha_A = C_A - C_A^e, \quad \alpha_B = C_B - C_B^e$$

If we assumed that when thermodynamic equilibrium is attained, X moles of A have been consumed to form X moles of B

$$\text{We then get } C_A^e = C_A - X \quad (1), \quad C_B^e = C_B + X \quad (2)$$

$$\Downarrow \quad (1) + (2)$$

$$C_A^e + C_B^e = C_A - X + C_B + X = C_A + C_B$$

$$\begin{aligned} \text{Thus, } \alpha_A + \alpha_B &= C_A - C_A^e + C_B - C_B^e \\ &= (C_A + C_B) - (C_A^e + C_B^e) = 0 \end{aligned}$$

$$\text{Hence } \alpha_A = -\alpha_B$$