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.

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

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

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

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.

@ Equilibrium, $J_{ch} = -\frac{dC_A}{dt} = \frac{dC_B}{dt} = 0$

↑

Macroscopic chemical reaction rate

Hence, we can write

$$k_1 C_A^e = k_{-1} C_B^e$$

→ refers to equilibrium condition

$$\downarrow$$

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

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

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

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

We then get $\quad C_A^e = C_A - x \quad , \quad C_B^e = C_B + x$
①   ②

$$\Downarrow \text{①+②}$$

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

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

$$= (C_A + C_B) - (C_A^e + C_B^e) = 0$$

Hence $\quad \alpha_A = -\alpha_B$