Day-13

→ Pressure dependence of rate of reaction –

$$a\,\text{Fuel} + b\,O_2 \longrightarrow c\,\text{Products}$$
(global reaction)

$$\text{Rate of reaction} = A_0 \exp.\left(\frac{-E_A}{R_u T}\right)[\text{Fuel}]^n[O_2]^m$$

$$= A_0 \exp.\left(\frac{-E_A}{R_u T}\right)\left(\frac{\chi_{fuel} P_T}{R_u T}\right)^n \left(\frac{\chi_{O_2} P_T}{R_u T}\right)^m$$

[using $PV = NR_uT$

$$\Rightarrow \frac{N}{V} = \frac{P}{R_u T}$$

so $[\text{Fuel}] = \frac{P_{fuel}}{R_u T} = \frac{\chi_{fuel} P_{total}}{R_u T}$]

$$= A_0 \exp.\left(\frac{-E_A}{R_u T}\right) \chi_{fuel}^n \chi_{O_2}^m \left(\frac{P_{Total}}{R_u T}\right)^{n+m}$$

→ Trimolecular reaction –

$$H + H + m \longrightarrow H_2 + M$$

$$A(g) + B(g) + \underbrace{Pt(s)}_{\text{Solid catalyst not considered in molecularity of reac}^n\text{, since its molecules actually don't collide.}} \longrightarrow AB(g) + Pt(s)$$

→ multi-step:

$$H_2 + O_2 \underset{k_{r_1}}{\overset{k_{f_1}}{\rightleftharpoons}} HO_2 + H \qquad (R_1)$$

$$H + O_2 \underset{k_{r_2}}{\overset{k_{f_2}}{\rightleftharpoons}} OH + H \qquad (R_2)$$

$$\frac{d[O_2]}{dt} = -k_{f_1}[H_2][O_2] + k_{r_1}[HO_2][H] - k_{f_2}[H][O_2] + k_{r_2}[OH][H]$$

General:

$$aA + bB \underset{k_r}{\overset{k_f}{\rightleftharpoons}} cC + dD \quad \text{(elementary reactions)}$$

$$\frac{1}{a}\frac{d[A]}{dt} = -k_f[A]^a[B]^b + k_r[C]^c[D]^d$$

At equilibrium, $\frac{d[A]}{dt} = 0$

$$\Rightarrow k_f[A]^a[B]^b = k_r[C]^c[D]^d$$

$$\Rightarrow \frac{k_f}{k_r} = \frac{[C]^c[D]^d}{[A]^a[B]^b} = k_c$$

↓ Equilibrium constant based on conc^n

$$k_p = \frac{(P_c/P_0)^c(P_d/P_0)^d}{(P_a/P_0)^a(P_b/P_0)^b}$$

$$= \frac{\left(\frac{[C]R_vT}{P_0}\right)^c\left(\frac{[D]R_vT}{P_0}\right)^d}{\left(\frac{[A]R_vT}{P_0}\right)^a\left(\frac{[B]R_vT}{P_0}\right)^b}$$

$$\Rightarrow K_p = K_c \left(\frac{R_u T}{P_0}\right)^{c+d-(a+b)}$$

$$= \frac{k_f}{k_r} \left(\frac{R_u T}{P_0}\right)^{\Delta n_g}$$

→ $NO + O \longrightarrow N + O_2$

$$k_f = 3.8 \times 10^9 \, T \exp.\left(\frac{-20820}{T}\right) \text{ cm}^3/\text{mol-s}$$

$T = 2300$ K, find k_r.

Ans:) $K_c = K_p$

$$\Rightarrow k_r = \frac{k_f}{K_p}$$

$$K_p = \exp.\left(\frac{61243 + 101627 - 326331 - 0}{8.314 \times 2300}\right)$$

$$= 1.94 \times 10^{-4}$$

$$k_f = 3.8 \times 10^9 \times 2300 \, e\left(\frac{-20820}{2300}\right)$$

$$= 1.024 \times 10^9$$

So $$k_r = \frac{1.024 \times 10^9}{1.94 \times 10^{-4}}$$

$$= 0.5278 \times 10^{13}$$

$$= 5.278 \times 10^{12} \text{ cm}^3/\text{mol-s}$$