1 Thermodynamics

$\xi \equiv \frac{n_i - n_{i0}}{\nu_i} = -\frac{X_A n_{A0}}{\nu_A} \qquad \xi_\mathrm{e} \equiv -\frac{X_\mathrm{e} n_{A0}}{\nu_A} \qquad \breve{\xi} \equiv \frac{\xi}{V}$

$n_A = n_{A0} + \nu_A \xi = n_{A0}(1-X) = 1 - \frac{n_i}{n_{i0}}$

$K_a = \prod_i a_i^{\nu_i} = e^{-\frac{\Delta G^\ominus}{RT}} \qquad K_P = \prod_i p_i^{\nu_i}$

$\frac{\mathrm{d}\ln k}{\mathrm{d}T} = \frac{E}{RT^2} \qquad \frac{\mathrm{d}\ln k}{\mathrm{d}T^{-1}} = -\frac{E}{R} \; \Delta_\mathrm{r} G^\circ = \sum_i \nu_i \Delta G_i^\circ$

$\Delta G^\circ = \sum_i \nu_i \mu_i^\circ = -RT \sum_i \nu_i \ln a_i = -RT \ln K_a$

$\left[\frac{\partial(\Delta G^\circ / T)}{\partial T}\right]_P = \frac{-\Delta_\mathrm{r} H}{T^2}$

1.1 Properties of Gases

Ideal: $a_i = p_i$ Real: $a_i = \frac{f_i^\star}{f_i^{\star\circ}}$

$a_i = f_i = y_i f_i^\star = y_i P \phi_i$

$K_a = K_p K_\phi \qquad K_P = K_y P^{\bar{\nu}} \qquad \bar{\nu} = \sum_i \nu_i$

1.2 Properties of Liquids

Ideal: $a_i = x_i$ Real: $a_i = x_i \gamma_i$

$\left(\frac{\mathrm{d}\ln K_a}{\mathrm{d}T}\right)_P = \frac{\Delta H^\circ}{RT^2} \to \left[\frac{\mathrm{d}\ln K_a}{\mathrm{d}(1/T)}\right]_P = -\frac{\Delta H^\circ}{R}$

2 Rate Law

$k = A\mathrm{e}^{-\frac{E_\mathrm{a}}{RT}} \qquad \breve{r} = \breve{r}_\mathrm{fwd} - \breve{r}_\mathrm{rev} \qquad \breve{r} = k \prod_i c_i^{\alpha_i} \qquad \overline{\alpha} = \sum_i \alpha_i$

Order	Rate	Formula
0	$\breve{r} = k$	$c_{A0} - c_A = kt$
1	$\breve{r} = kc_A$	$\ln \frac{c_{A0}}{c_A} = kt$
2-I	$\breve{r} = kc_A^2$	$c_A^{-1} - c_{A0}^{-1} = kt$
2-II	$\breve{r} = kc_A c_B$	$\ln \frac{c_{A0}}{c_{B0}} + \ln \frac{c_B}{c_A} = (c_{A0}\nu_B - c_{B0}\nu_A)kt$
3-I	$\breve{r} = kc_A^3$	$c_{A0}^{-2} - c_A^{-2} = 2\nu_A kt$
3-II	$\breve{r} = kc_A^2 c_B$	$c_A^{-1} - c_{A0}^{-1} + (c_{A0} - c_{B0}\frac{\nu_A}{\nu_B})^{-1} \ln \frac{c_B c_{A0}}{c_A c_{B0}}$ $= (c_{A0}\nu_B - c_{B0}\nu_A)kt$
3-III	$\breve{r} = kc_A c_B c_Q$	$\nu_A(\nu_Q c_{B0} - \nu_A c_{Q0}) \ln \frac{c_A}{c_{A0}}$ $+\nu_B(\nu_A c_{Q0} - \nu_Q c_{A0}) \ln \frac{c_B}{c_{B0}}$ $+\nu_Q(\nu_B c_{A0} - \nu_A c_{B0}) \ln \frac{c_Q}{c_{Q0}}$ $= kt(\nu_A c_{B0} - \nu_B c_{A0})(\nu_A c_{Q0} - \nu_Q c_{A0})$ $\times(\nu_Q c_{B0} - \nu_B c_{Q0})$
n	$\breve{r} = k \prod_i c_i^{\alpha_i}$	$(c_A^{n-1})^{-1} - (c_{A0}^{n-1}) = (1-n)\nu_A kt$

$\varepsilon_A \equiv \frac{V|_{X_A=1} - V|_{X_A=0}}{V|_{X_A=0}} = \frac{n_\mathrm{T}|_{X_A=1} - n_\mathrm{T}|_{X_A=0}}{n_\mathrm{T}|_{X_A=0}}$

$\breve{r} = [V_0(1+\varepsilon_A X_A)]^{-1}\left(-\frac{n_{A0}}{\nu_A}\frac{\mathrm{d}X_A}{\mathrm{d}t}\right) = -\frac{c_{A0}}{1+\varepsilon_A X_A}\frac{1}{\nu_A}\frac{\mathrm{d}X_A}{\mathrm{d}t}$

$\breve{r} = \frac{1}{V}\frac{\mathrm{d}\xi}{\mathrm{d}t} = \frac{1}{V\nu_i}\frac{\mathrm{d}n_i}{\mathrm{d}t} = \frac{1}{\nu_i}\frac{\mathrm{d}c_i}{\mathrm{d}t} + \frac{c_i}{V\nu_i}\frac{\mathrm{d}V}{\mathrm{d}t}$

$N(t) = N_0 0.5^{\frac{t}{t_{1/2}}} = N_0 e^{-\frac{t}{\tau}} = N_0 e^{-\lambda t}$

Order	0	1	2	3	n
$t_{1/2}$	$-\frac{c_{A0}}{2\nu_A k}$	$\frac{\ln 2}{k}$	$-\frac{1}{\nu_A k c_{A0}}$	$-\frac{3}{2\nu_A k c_{A0}^2}$	$\frac{2^{n-1}-1}{(1-n)\nu_A k c_{A0}^{n-1}}$

3 Molecular Kinetics

$\breve{Z}_{AA} = 2(\rho_{N,A})^2 \sigma_A^2 \sqrt{\frac{\pi k_\mathrm{B} T}{\breve{m}}} \qquad \breve{Z}_{AB} = \rho_{N,A}\rho_{N,B}\pi\sigma_{AB}^2 \sqrt{\frac{8 k_\mathrm{B} T}{\pi \mu_{AB}}}$

$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2} \qquad \mu_{AB} = \frac{\breve{m}_A \breve{m}_B}{\breve{m}_A + \breve{m}_B}$

$\breve{r}_{AB} = \rho_\mathrm{s} \breve{Z}_{AB} e^{\frac{-E_\mathrm{a}}{RT}} = k\rho_{N,A}\rho_{N,B}$

4 Multiple Reactions

$K_\mathrm{e} = \frac{k_\mathrm{fwd}}{k_\mathrm{rev}} = \frac{c_{B\mathrm{e}}}{c_{A\mathrm{e}}} \qquad \breve{r}_\mathrm{e} = k_\mathrm{fwd} - k_\mathrm{rev} = 0$

$A \underset{k_\mathrm{rev}}{\overset{k_\mathrm{fwd}}{\rightleftharpoons}} B: \; \breve{r} = k_\mathrm{fwd} c_A - k_\mathrm{rev} c_B$

$$-(k_\mathrm{fwd} + k_\mathrm{rev})t = \ln \frac{K_\mathrm{e} c_A - c_B}{K_\mathrm{e} c_{A0} - c_{B0}} = \ln \frac{\frac{c_{B\mathrm{e}} c_A}{c_{A0}} - c_B}{\frac{c_{B\mathrm{e}} c_{A0}}{c_{A\mathrm{e}}} - c_{B0}}$$

$A + B \underset{k_\mathrm{rev}}{\overset{k_\mathrm{fwd}}{\rightleftharpoons}} R + S: \; \breve{r} = k_\mathrm{fwd} c_A c_B - k_\mathrm{rev} c_R c_S$

$0 = K_\mathrm{e}(c_{A0} - \breve{\xi}_\mathrm{e})(c_{B0} - \breve{\xi}_\mathrm{e}) - (c_{R0} + \breve{\xi}_\mathrm{e})(c_{S0} + \breve{\xi}_\mathrm{e})$

$\zeta \equiv k_\mathrm{fwd}(c_{A\mathrm{e}} + c_{B\mathrm{e}}) + k_\mathrm{rev}(c_{R\mathrm{e}} + c_{S\mathrm{e}})$

$\Delta\xi = \breve{\xi} - \breve{\xi}_\mathrm{e}$

$t = \zeta^{-1} \ln\left(k_\mathrm{fwd} - k_\mathrm{rev} - \frac{\zeta}{\Delta\xi}\right)$

$A + B \underset{k_\mathrm{rev}}{\overset{k_\mathrm{fwd}}{\rightleftharpoons}} R: \; \breve{r} = k_\mathrm{fwd} c_A c_B - k_\mathrm{rev} c_R$

$\breve{\xi}_\mathrm{e} = \frac{K_\mathrm{e}(c_{A0} + c_{B0}) + 1 + \sqrt{\zeta}}{2K_\mathrm{e}}$

$\zeta \equiv K_\mathrm{e}^2(c_{A0} - c_{B0})^2 + 2K_\mathrm{e}(c_{A0} + c_{B0} + 2c_{R0}) + 1$

$\Delta\xi = \breve{\xi} - \breve{\xi}_\mathrm{e}$

$[k_\mathrm{fwd}(c_{A\mathrm{e}} + c_{B\mathrm{e}}) + k_\mathrm{rev}]t =$

$\ln \frac{\breve{\xi}_\mathrm{e}\left[K_\mathrm{e}\Delta\xi - (K_\mathrm{e}[c_{A\mathrm{e}} + c_{B\mathrm{e}}] + 1)\right]}{\Delta\xi[K_\mathrm{e}\breve{\xi}_\mathrm{e} + K_\mathrm{e}(c_{A\mathrm{e}} + c_{B\mathrm{e}}) + 1]}$

$A \overset{k_1}{\underset{k_2}{\rightrightarrows}} \begin{matrix} R \\ T \end{matrix}: \; \breve{\xi}_1 = \frac{k_1 c_{A0}}{k_1 + k_2}\left(e^{-[k_1+k_2]t}\right) \qquad \breve{\xi}_2 = \frac{k_2 c_{A0}}{k_1 + k_2}\left(e^{-[k_1+k_2]t}\right)$

$c_A = c_{A0}\left(e^{-[k_1+k_2]t}\right) \qquad \frac{c_R - c_{R0}}{c_T - c_{T0}} = \frac{k_1}{k_2}$

5 Catalysis

$K_\mathrm{cat} = \frac{k_\mathrm{ad}}{k_\mathrm{de}} \qquad \theta_\mathrm{v} = 1 - \sum_i \theta_i$

5.1 Single Species

$\breve{r}_\mathrm{ad} = k_\mathrm{ad} p_A(1 - \theta_A) \qquad \breve{r}_\mathrm{de} = k_\mathrm{de}\theta_A$

$\theta_A = \frac{k_\mathrm{ad} p_A}{k_\mathrm{de} + k_\mathrm{ad} p_A} = \frac{K_\mathrm{cat} p_A}{1 + K_\mathrm{cat} p_A}$

5.2 Multiple Species

$A + B \underset{k_\mathrm{de}}{\overset{k_\mathrm{ad}}{\rightleftharpoons}} R + S \qquad \theta_\mathrm{v} = 1 - \sum_i \theta_i$

$k_{\mathrm{ad},A}\theta_A\theta_B = k_{\mathrm{de},A}\theta_R\theta_S \qquad \theta_A = \frac{\theta_R\theta_S}{K_{\mathrm{cat},A}\theta_B}$

$k_{\mathrm{ad},B} p_B \theta_\mathrm{v} = k_{\mathrm{de},B}\theta_B \qquad \theta_B = K_{\mathrm{cat},B} p_B \theta_\mathrm{v}$

$\theta_R = K_{\mathrm{cat},R} p_R \theta_\mathrm{v} \qquad \theta_S = K_{\mathrm{cat},S} p_S \theta_\mathrm{v}$

$\hat{r} = k_{\mathrm{ad},A}\left(p_A\theta_\mathrm{v} - \frac{\theta_A}{K_{\mathrm{cat},A}}\right)$

5.3 Dissociation Occurs on Adsorption

$\breve{r}_\mathrm{ad} = k_{\mathrm{ad},A} p_A \theta_\mathrm{v}^2 = k_{\mathrm{ad},A}(1 - \theta_A)^2 \qquad \breve{r}_\mathrm{de} = k_{\mathrm{de},A}\theta_A^2$

$\theta_A = \frac{\sqrt{K_{\mathrm{cat},A} p_A}}{1 + \sqrt{K_{\mathrm{cat},A} p_A}}$

Only A dissociates: $\theta_A = \frac{\sqrt{K_{\mathrm{cat},A} p_A}}{1 + \sqrt{K_{\mathrm{cat},A} p_A} + K_{\mathrm{cat},B} p_B + K_{\mathrm{cat},C} p_C}$

6 Reactor Design

6.1 Batch Reactor

$t = c_{A0}\int_0^{X_A} \frac{dX_A}{-\breve{r}_A} = -\int_{c_{A0}}^{c_A} \frac{dc_A}{-\breve{r}_A}$

$t = n_{A0}\int_0^{X_A} \frac{dX_A}{-\breve{r}_A V_0(1 + \varepsilon_A X_A)} = c_{A0}\int_0^{X_A} \frac{dX_A}{-\breve{r}_A(1 + \varepsilon_A X_A)}$

$c_A = c_{A0}(1 - X_A) \qquad c_Z = c_{Z0} + c_{A0} X_A$

6.2 Plug Flow Reactor

$\frac{V}{F_{A0}} = \int_{X_{A,\mathrm{in}}}^{X_{A,\mathrm{out}}} \frac{dX_A}{-\breve{r}_A} \qquad \tau = \frac{V}{V_0} = c_{A0}\int_{X_{A,\mathrm{in}}}^{X_{A,\mathrm{out}}} \frac{dX_A}{-\breve{r}_A}$

$\{\varepsilon = 0\}: \tau = -\int_{c_{A,\mathrm{in}}}^{c_{A,\mathrm{out}}} \frac{dc_A}{-\breve{r}_A}$

Gas: $c_A = c_{A0}\frac{1 - X_A}{1 + \varepsilon_A X_A}$

$t_\mathrm{m} = \int_{X_{A,\mathrm{in}}}^{X_{A,\mathrm{out}}} \frac{F_{A0} dX_A}{-\breve{r}_A V_0(1 + \varepsilon_A X_A)} = c_{A0}\int_{X_{A,\mathrm{in}}}^{X_{A,\mathrm{out}}} \frac{dX_A}{-\breve{r}_A(1 + \varepsilon_A X_A)}$

6.3 CSTR

$\frac{V}{F_{A0}} = \frac{X_{A,\text{out}} - X_{A,\text{in}}}{-\breve{r}_{A,\text{out}}}$

$\tau = \frac{c_{A0}}{-\breve{r}_{A,\text{out}}}(X_{A,\text{out}} - X_{A,\text{in}}) = \frac{c_{A0}}{-\breve{r}_{A,\text{out}}}\int\limits_{X_{A,\text{in}}}^{X_{A,\text{out}}} dX_A$

$\tau = \frac{1}{-\breve{r}_{A,\text{out}}}(c_{A,\text{out}} - c_{A,\text{in}}) = \frac{1}{-\breve{r}_{A,\text{out}}}\int\limits_{c_{A,\text{in}}}^{c_{A,\text{out}}} dc_A$

6.4 PFR Recycle Reactor

$\frac{V}{F_{A0}} = (R+1)\int\limits_{RX_{A,\text{PFR out}}/(R+1)}^{X_{A,\text{PFR out}}} \frac{dX_A}{-\breve{r}_A}$ $\qquad X_{A,\text{PFR in}} = \frac{R}{R+1}X_{A,\text{PFR out}}$

$R \equiv \frac{\text{volume of fluid returned}}{\text{volume of fluid leaving in net product}}$

7 Temperature and Energy Effects

Batch: $\dot{Q} = \breve{r}V\Delta_\text{r}H + \sum\left(n_i\bar{C}_{P,i}\frac{\mathrm{d}T}{\mathrm{d}t}\right)$ $\qquad T = T_0 + \frac{\Delta_\text{r}H(T_0)n_{A0}X_A}{\nu_A\sum(n_i\bar{C}_{P,i})}$

CSTR: $\dot{Q} = \frac{F_{A0}(X_{A,\text{out}} - X_{A,\text{in}})}{-\nu_A}\Delta_\text{r}H(T_0) + \sum\left(F_i\int\limits_{T_0}^{T_\text{out}}\bar{C}_{P,i}\,dT\right)$

Tubular reactor: $\int\limits_{X_{A,\text{in}}}^{X_{A,\text{out}}} U\Delta T\frac{4}{\varnothing}F_{A0}\frac{dX_A}{-\breve{r}_A} =$

$$\sum\left(F_i\int\limits_{T_0}^{T}\bar{C}_{P,i}\,dT\right) - \frac{F_{A0}\Delta_\text{r}H(T_0)}{\nu_A}(X_{A,\text{out}} - X_{A,\text{in}})$$

8 Deviation from Ideal Flow

$t_\text{m} = t = \int\limits_{t=0}^{t=\infty} t\left(\frac{\mathrm{d}F(t)}{\mathrm{d}t}\right)\,dt$

References

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