

## 1. Fundamentals of Thermodynamics:

$$dU = dQ + dW; \quad dW = -PdV; \quad C_v = \left( \frac{\partial U}{\partial T} \right)_V; \quad C_p = \left( \frac{\partial H}{\partial T} \right)_P;$$

$$C_p - C_v = R; \quad TV^{\gamma-1} = \text{const}; \quad TP^{\frac{1-\gamma}{\gamma}} = \text{const}; \quad PV^\gamma = \text{const}$$

$$dH = dU + d(PV); \quad dS = \frac{dQ}{T}; \quad PV = nRT$$

## 2. Volumetric Properties of Pure Fluids:

$$\Psi = 2 + \mathcal{C} - \mathcal{P} - \mathcal{R}; \quad \beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P; \quad \kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T; \quad T_r = \frac{T}{T_c}; \quad P_r = \frac{P}{P_c}; \quad PV = ZRT$$

$$Z = 1 + \frac{BP}{RT} = 1 + \frac{BP_c}{RT_c} \frac{P_r}{T_r}; \quad \frac{BP_c}{RT_c} = B^0 + \omega B^1; \quad B^0 = 0.083 - \frac{0.422}{T_r^{1.6}}; \quad B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

$$P = \frac{RT}{V-b} - \frac{a}{V^2}; \quad a = \frac{27}{64} \frac{R^2 T_c^2}{P_c}; \quad b = \frac{1}{8} \frac{RT_c}{P_c}; \quad [\text{van der Waals (vdW) EOS}]$$

$$P = \frac{RT}{V-b} - \frac{a}{V\sqrt{T}(V+b)}; \quad a = \frac{0.42748R^2 T_c^2}{P_c}; \quad b = \frac{0.08664RT_c}{P_c}; \quad [\text{Redlich-Kwong (RK) EOS}]$$

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V(V+b)}; \quad a = \frac{0.427R^2 T_c^2}{P_c}; \quad b = \frac{0.08664RT_c}{P_c} \quad \text{and}$$

$$\alpha = \left[ 1 + (0.480 + 1.574\omega - 0.176\omega^2) (1 - \sqrt{T_r}) \right]^2; \quad [\text{Soave-Redlich-Kwong (SRK) EOS}]$$

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V(V+b) + b(V-b)}; \quad a = \frac{0.45274R^2 T_c^2}{P_c}; \quad b = \frac{0.07780RT_c}{P_c}; \quad \text{and}$$

$$\alpha = \left[ 1 + \kappa (1 - \sqrt{T_r}) \right]^2; \quad \kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2; \quad [\text{Peng-Robinson (PR) EOS}]$$

$$Z_{\text{vap}} = 1 + \beta - q\beta \frac{Z_{\text{vap}} - \beta}{(Z_{\text{vap}} + \varepsilon\beta)(Z_{\text{vap}} + \sigma\beta)}; \quad [\text{Vapour \& Vapour-like Roots}]$$

$$Z_{\text{liq}} = 1 + \beta + (Z_{\text{liq}} + \varepsilon\beta)(Z_{\text{liq}} + \sigma\beta) \left( \frac{1 + \beta - Z_{\text{liq}}}{q\beta} \right); \quad [\text{Liquid \& Liquid-like Roots}]$$

$$\beta = \Omega \frac{P_r}{T_r}; \quad q = \frac{\Psi\alpha}{\Omega T_r}; \quad \alpha_{\text{SRK}} = \left[ 1 + (0.480 + 1.574\omega - 0.176\omega^2) (1 - \sqrt{T_r}) \right]^2; \quad \text{and}$$

$$\alpha_{\text{PR}} = \left[ 1 + (0.37464 + 1.54226\omega - 0.26992\omega^2) (1 - \sqrt{T_r}) \right]^2$$

EOS	$\alpha$	$\sigma$	$\varepsilon$	$\Omega$	$\Psi$
vdW	1	0	0	1/8	27/64
RK	$T_r^{-1/2}$	1	0	0.08664	0.42748
SRK	$\alpha_{\text{SRK}}$	1	0	0.08664	0.42748
PR	$\alpha_{\text{PR}}$	$1+\sqrt{2}$	$1-\sqrt{2}$	0.07780	0.45724

Table 1: Parameters for the generic form of cubic equations of state.

$$Z_{\text{vap}}^{(i+1)} = Z_{\text{vap}}^{(i)} - \frac{F(Z_{\text{vap}}^{(i)})}{F'(Z_{\text{vap}}^{(i)})}; \quad (\text{Root-finder expression for the Newton-Raphson method})$$

## 3. Thermodynamic Properties of Pure Fluids:

$$\begin{aligned}
H &= U + PV; \quad G = H - TS; \quad A = U - TS; \\
dU &= TdS - PdV; \quad dH = TdS + VdP; \quad dA = -PdV - SdT; \quad dG = VdP - SdT; \\
\left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial P}{\partial S}\right)_V; \quad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P; \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V; \quad \text{and} \\
-\left(\frac{\partial S}{\partial P}\right)_T &= \left(\frac{\partial V}{\partial T}\right)_P; \quad (\text{Maxwell relations}) \\
\left(\frac{\partial U}{\partial S}\right)_V &= T = \left(\frac{\partial H}{\partial S}\right)_P; \quad \left(\frac{\partial U}{\partial V}\right)_S = -P = \left(\frac{\partial A}{\partial V}\right)_T; \quad \left(\frac{\partial H}{\partial P}\right)_S = V = \left(\frac{\partial G}{\partial P}\right)_T; \quad \text{and} \\
\left(\frac{\partial A}{\partial T}\right)_V &= -S = \left(\frac{\partial G}{\partial T}\right)_P \\
dH &= C_p dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP; \quad dS = C_p \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP; \\
dU &= C_v dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV; \quad dS = \frac{C_v}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV; \\
d\left(\frac{G}{RT}\right) &= \frac{V}{RT} dP - \frac{H}{RT^2} dT \quad (\text{Generating function}); \\
M^R &= M - M^{\text{ig}}; \quad \frac{H^R}{RT} = -T \int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P}; \quad \frac{S^R}{R} = -T \int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_0^P (Z-1) \frac{dP}{P}; \quad \text{and} \\
\frac{G^R}{RT} &= \int_0^P (Z-1) \frac{dP}{P} \quad (\text{Residual properties}); \\
\frac{dP^{\text{sat}}}{dT} &= \frac{\Delta H^{\alpha\beta}}{T\Delta V^{\alpha\beta}}; \quad \frac{d(\ln P^{\text{sat}})}{dT} = \frac{\Delta H^{\text{fg}}}{RT^2}; \quad (\text{Clapeyron relations}) \\
x^{(V)} &= \frac{M - M^{(L)}}{M^{(V)} - M^{(L)}} \quad (\text{Quality of vapour});
\end{aligned}$$

## 4. Vapour-Liquid Equilibrium of Mixtures:

$$\begin{aligned}
x_i &= \frac{n_i^{(L)}}{n}; \quad y_i = \frac{n_i^{(V)}}{n}; \quad \sum_{i=1}^c x_i = 1; \quad \sum_{i=1}^c y_i = 1 \quad (\text{Molar fraction of liquid and vapour phases}); \\
\bar{M}_i &= \left(\frac{\partial(nM)}{\partial n_i}\right)_{T,P,n_{j \neq i}} \quad (\text{Partial molar property}); \quad M^E = M - M^{\text{id}} \quad (\text{Excess properties}) \\
\mu_i &= \left(\frac{\partial(nG)}{\partial n_i}\right)_{T,P,n_{j \neq i}} = \bar{G}_i; \quad dG = VdP - SdT + \sum_i \mu_i dx_i; \\
P_i &= y_i P = x_i \gamma_i P_i^{\text{sat}} \quad (\text{Raoult's law}); \quad P = \sum_{i=1}^c P_i = \sum_{i=1}^c y_i P; \quad T_c^t = \sum_{i=1}^c y_i T_{c,i}; \quad P_c^t = \sum_{i=1}^c y_i P_{c,i}; \\
P_i &= y_i P = x_i \mathcal{H}_i \quad (\text{Henry's law}); \\
K_i &= \frac{P_i^{\text{sat}}}{P} = \frac{y_i}{x_i}; \quad F = V + L; \quad Fz_i = x_i L + y_i V; \quad \sum_{i=1}^c \frac{z_i K_i}{1 + V(K_i - 1)} = 1;
\end{aligned}$$

## 5. Solution Thermodynamics:

$$\begin{aligned}
RT \left( \frac{\partial \ln f}{\partial P} \right)_T &= \bar{v}; \quad \lim_{P \rightarrow 0} \frac{f}{P} = 1; \quad RT \ln \left( \frac{\bar{f}_i}{y_i f_i} \right) = \int_0^P (\bar{V}_i - \bar{v}_i) dP \\
\bar{f}_i^V &= y_i P' \quad \text{and} \quad \bar{f}_i^L = x_i f_i^L \quad (\text{Lewis-Randall relation}); \\
\mu_i - \mu_i^0 &= RT \ln \left( \frac{\bar{f}_i}{f_i^0} \right); \quad a_i = \frac{\bar{f}_i}{f_i^0}; \quad \gamma_i = \frac{a_i}{y_i} = \frac{\bar{f}_i}{x_i f_i}; \\
\phi_i &= \frac{f_i}{P}; \quad G_i^R = G_i - G_i^{\text{ig}} = RT \ln \left( \frac{f_i}{P} \right) = RT \ln \phi_i; \\
f_i^L(P) &= \phi_i^{\text{sat}} P_i^{\text{sat}} \exp \left[ \frac{V_i^L (P - P_i^{\text{sat}})}{RT} \right] \\
\left( \frac{\partial M}{\partial T} \right)_{P,x} dT + \left( \frac{\partial M}{\partial P} \right)_{T,x} dP - \sum_{i=1}^c x_i d\bar{M}_i &= 0 \quad (\text{Gibbs-Duhem equation}) \\
\sum_i x_i d\bar{M}_i &= 0; \quad \sum_i x_i \frac{d\bar{M}_i}{dx_j} = 0; \\
M^E &= M - \sum_i x_i M_i; \quad \bar{M}_1 = M + x_2 \frac{dM}{dx_1}; \quad \bar{M}_2 = M - x_1 \frac{dM}{dx_1} \\
x_1 \frac{d\bar{M}_1}{dx_1} + x_2 \frac{d\bar{M}_2}{dx_1} &= 0; \quad \frac{d\bar{M}_1}{dx_1} = -\frac{x_2}{x_1} \frac{d\bar{M}_2}{dx_1} \\
PV^{\text{igm}} &= \left( \sum_{i=1}^c n_i \right) RT; \quad \bar{V}_i^{\text{igm}}(T, P, y) = \frac{RT}{P} = \bar{V}_i^{\text{ig}}(T, P); \quad P_i^{\text{igm}} \left( \sum_{i=1}^c n_i, V, T, y \right) = \frac{n_i RT}{V} = P^{\text{ig}}(n_i, V, T); \\
\bar{U}^{\text{igm}}(T, y) &= \sum_{i=1}^c y_i \bar{U}_i^{\text{ig}}(T); \quad \bar{H}^{\text{igm}}(T, P, y) = \sum_{i=1}^c y_i \bar{H}_i^{\text{ig}}(T, P); \quad \bar{V}^{\text{igm}}(T, P, y) = \sum_{i=1}^c y_i \bar{V}_i^{\text{ig}}(T, P) \\
\bar{S}^{\text{igm}}(T, P, y) &= \sum_{i=1}^c y_i \bar{S}_i^{\text{ig}}(T, P) - R \sum_{i=1}^c y_i \ln y_i; \quad \bar{G}^{\text{igm}}(T, P, y) = \sum_{i=1}^c y_i \bar{G}_i^{\text{ig}}(T, P) + RT \sum_{i=1}^c y_i \ln y_i; \quad \text{and} \\
\bar{A}^{\text{igm}}(T, P, y) &= \sum_{i=1}^c y_i \bar{A}_i^{\text{ig}}(T, P) + RT \sum_{i=1}^c y_i \ln y_i \\
M^{\text{id}} &= \sum_i x_i \bar{M}_i^{\text{id}}; \quad V^{\text{id}} = \sum_i x_i V_i; \quad H^{\text{id}} = \sum_i x_i H_i; \quad S^{\text{id}} = \sum_i x_i S_i - R \sum_i x_i \ln x_i \quad \text{and} \\
G^{\text{id}} &= \sum_i x_i G_i - RT \sum_i x_i \ln x_i; \\
d \left( \frac{nG^E}{RT} \right) &= \frac{nV^E}{RT} dP - \frac{nH^E}{RT^2} dT + \sum_i \ln \gamma_i dn_i; \quad \frac{V^E}{RT} = \left( \frac{\partial \left( \frac{G^E}{RT} \right)}{\partial P} \right)_{T,x}; \quad \frac{H^E}{RT} = -T \left( \frac{\partial \left( \frac{G^E}{RT} \right)}{\partial T} \right)_{P,x}; \\
\ln \gamma_i &= \left( \frac{\partial \left( \frac{G^E}{RT} \right)}{\partial n_i} \right)_{T,P,n_j (n_j \neq n_i)}; \quad \bar{G}_i^E = RT \ln \gamma_i;
\end{aligned}$$

$$\ln \gamma_1 = x_2^2 [A_{12} + 2(A_{21} - A_{12})x_1]; \quad \ln \gamma_2 = x_1^2 [A_{21} + 2(A_{12} - A_{21})x_2]; \quad (\text{Margules activity model});$$

$$\ln \gamma_1 = B_{12} \left(1 + \frac{B_{12}x_1}{A_{21}x_2}\right)^{-2}; \quad \ln \gamma_2 = B_{21} \left(1 + \frac{B_{21}x_1}{A_{12}x_2}\right)^{-2}; \quad (\text{Van Laar activity model});$$

$$\frac{G^E}{RT} = x_1 \ln(x_1 + x_2 C_{12}) - x_2 \ln(x_2 + x_1 C_{21}) \quad \text{with}$$

$$\ln \gamma_1 = -\ln(x_1 + x_2 C_{12}) + x_2 \left( \frac{C_{12}}{x_1 + x_2 C_{12}} - \frac{C_{21}}{x_2 + x_1 C_{21}} \right) \quad \text{and}$$

$$\ln \gamma_2 = -\ln(x_2 + x_1 C_{21}) + x_1 \left( \frac{C_{12}}{x_1 + x_2 C_{12}} - \frac{C_{21}}{x_2 + x_1 C_{21}} \right);$$

## 6. Chemical Reaction Equilibrium:

$$\sum_{i=1}^C \nu_i A_i = 0; \quad d\epsilon = \frac{dn_i}{\nu_i}; \quad \sum_i n_i = \sum_i n_{i0} + \epsilon \sum_i \nu_i; \quad n = n_0 + \nu\epsilon$$

$$y_i = \frac{n_i}{n} = \frac{n_{i0} + \nu_i \epsilon}{n_0 + \nu \epsilon}$$

$$\sum_i \nu_i G_i = \sum_i \nu_i \mu_i = 0; \quad \prod_i \left( \frac{\bar{f}_i}{f_i^0} \right)^{\nu_i} = \prod_i a_i^{\nu_i} = K = \exp \left( \frac{-\Delta G^0}{RT} \right);$$

$$\Delta H^0 = -RT^2 \frac{d}{dT} (\Delta G^0 / RT) \quad (\text{Standard heat of reaction});$$

$$\frac{d(\ln K)}{dT} = \frac{\Delta H^0}{RT^2} \quad (\text{Van't Hoff equation});$$

$$\prod_i (y_i \phi_i)^{\nu_i} = K \left( \frac{P}{P^0} \right)^{-\nu}, \quad \text{where } \nu = \sum_i \nu_i \quad (\text{gas-phase});$$

$$\prod_i (y_i \gamma_i)^{\nu_i} = K \exp \left[ \frac{P^0 - P}{RT} \sum_i (\nu_i V_i) \right]^{-\nu} \quad (\text{liquid-phase});$$

$$\prod_i (y_i)^{\nu_{i,j}} = \left( \frac{P}{P^0} \right)^{-\nu_{i,j}} K_j; \quad (\text{ideal gas multi-reaction})$$