Introductory Chemical Engineering Thermodynamics

Chapter 9 - Introduction to Multicomponent Systems

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INTRODUCTION TO MULTICOMPONENT SYSTEMS

The primary difference between pure and multicomponent systems is that we must now consider the impacts of changing the composition on the Gibbs energy. Beyond that, the Gibbs energy must still be minimized, the calculus of classical thermodynamics must be applied, the fugacities of the components in the phases must be equal, and, in general, the problem is pedagogically the same as the phase equilibrium problem for pure components. The computational methodology gets more complicated because there is more to keep track of. And the best choice of "equation of state" can change quite a bit depending on the nature of the solution. In this context, "equation of state" refers to any model equation for the thermodynamic properties of mixtures. But computations and equation of state development should not seem unfamiliar at this stage in the course.

eg. $d\underline{U}(T,P,n) = (\partial\underline{U}/\partial P)_{T,n}dP + (\partial\underline{U}/\partial T)_{P,n}\,dT + \textbf{S}\,(\partial\underline{U}/\partial n_i)_{P,T,n_{j\neq i}}\,dn_i$

eg. $d\underline{G}(T,P,n) = (\partial\underline{G}/\partial P)_{T,n}dP + (\partial\underline{G}/\partial T)_{P,n}\,dT + \textbf{S}\,(\partial\underline{G}/\partial n_i)_{P,T,n_{j\neq i}}\,dn_i$

At constant moles of material, the mixture must follow the same constraints as any other fluid. That is, we only have two state variables left if we keep the composition constant.

$\Rightarrow (\partial\underline{G}/\partial P)_{T,n} = \underline{V}$ and $(\partial\underline{G}/\partial T)_{p,n} = -\underline{S}$; Fundamental properties

therefore $d\underline{G} = \underline{V}dP - \underline{S}dT + \textbf{S}\,(\partial\underline{G}/\partial n_i)_{T,P,n_{j\neq i}}\,dn_i$

$\textbf{m}_i \equiv (\partial\underline{G}/\partial n_i)_{T,P,n_{j\neq i}} \equiv$ "chemical potential"

Equilibrium Constraint: equality of chemical potentials

$d\underline{G} = 0 = \Sigma\ \mu_i\ dn_i$ equilibrium, **constant T and P**

Define system of two components (eg. $EtOH+H_2O$) between two phases (eg. vapor and liquid).

$$m_1^L\,dn_1^L + m_2^L\,dn_2^L + m_1^V\,dn_1^V + m_2^V\,dn_2^V = 0$$

but if component 1 leaves the liquid phase then it must enter the vapor phase (and similarly for component 2).

$$\Rightarrow dn_1^L = -dn_1^V \text{ and } dn_2^L = -dn_2^V$$

$$\Rightarrow \left(m_1^V - m_1^V \right)dn_1^V + \left(m_2^V - m_2^L \right)dn_2^V = 0$$

Therefore,

$$m_1^V = m_1^L \text{ and } m_2^V = m_2^L.$$

Chemical potential of a pure fluid

$$\mu_j\big|_{n_i \to n} \equiv \left(\partial\underline{G}/\partial n_i\right)_{T,P,n_{j\neq i}}\Big|_{n_i \to n} = \left(\partial(nG)/\partial n_i\right)\big|_{n_i \to n} = G(\partial n/\partial n_i) + n(\partial G/\partial n_i)\big|_{n_i \to n}$$

but $n(\partial\underline{G}/\partial n_i)\big|_{n_i \to n} = n(\partial G/\partial n)$ and $G = G(T,P) \neq f(n) \Rightarrow n(\partial G/\partial n) = 0.$

Therefore, $\mu_j\big|_{n_i \to n} = G$

Note: This means $G^L = G^V$ for pure fluid, as before.

Thus, m_i is a "generalized G" for components in mixtures.

Equilibrium Constraint: equality of fugacities

Fugacity - "escaping tendency"

For a pure fluid:

$\ln(f/P) \equiv (G - G^{ig})/RT$

For mixtures, generalize:

$\ln(f/P) \equiv (G - G^{ig})/RT$ to $RT\ln(\hat{f}_i/P) \equiv (\mu_i - \mu_i^{ig})$

where $\hat{f}_i$ fugacity of component i in a mixture.

Equality of fugacities as a criterion of phase equilibrium

$\mu_i^V \left(T^{eq}, P^{eq} \right) = \mu_i^L \left(T^{eq}, P^{eq} \right)$

By definition, $\mu_i^V \left(T^{eq}, P^{eq} \right) - \mu_i^L \left(T^{eq}, P^{eq} \right) = RT \ln\left[\hat{f}_i^V \left(T^{eq}, P^{eq} \right) / \hat{f}_i^L \left(T^{eq}, P^{eq} \right) \right]$

but, $\mu_i^V \left(T^{eq}, P^{eq} \right) - \mu_i^L \left(T^{eq}, P^{eq} \right) = 0 \Rightarrow \ln\left(\hat{f}_i^V / \hat{f}_i^L \right) = 0$

$\hat{f}_i^V = \hat{f}_i^L$ at equilibrium.

Activity, Activity Coefficient, and Fugacity Coefficient

"Activity" $a_i = \hat{f}_i / f_i^{\circ}$ Ionic solutions, reactions

"Activity coefficient" $= g_i = \hat{f}_i / (x_i f_i^{\circ})$ Low pressure phase equilibria

"Fugacity coefficient" $= f_i = \hat{f}_i / (x_i P)$ High pressure phase equilibria

where f_i° is the value of the fugacity at standard state. The most common standard state is the pure component at the same temperature and pressure as the system of interest. In that case $f_i^{\circ} = f_i$. Note that the defining equation for activity coefficient can be rearranged to become an equation for calculating the fugacity of a component in a mixture. This is the general procedure used for liquids.

$$\hat{f}_i^{\,L} = \gamma_i x_i f_i^{\,o} = \gamma_i x_i f_i^{\,o} \equiv \gamma_i x_i \phi_i P$$

IDEAL SOLUTIONS

The simplest solution model is to assume that interaction energiess in the mixture are like interaction energies in the pure fluid. e.g. $^{35}Cl_2$ mixed with $^{37}Cl_2$

then, $\Delta H_{mix}^{is} = 0$ and $\underline{H}_{Tot}^{is} = \Sigma\, n_i\, H_i$

As for the entropy change of mixing, the loss of order due to mixing is unavoidable

$\Delta S_{mix}^{is} / R = -\Sigma\, x_i\, ln\,(\,x_i\,)$

Combining $\Rightarrow$ $\dfrac{\Delta G_{mix}^{is}}{RT} = \dfrac{\Delta H_{mix}^{is}}{RT} - \dfrac{\Delta S_{mix}^{is}}{R} = +\sum x_i\, ln(\,x_i\,)$

The definition of fugacity in terms of a change in free energies gives:

$\dfrac{\Delta G_{mix}}{RT} = \sum \dfrac{n_i}{n}\ \dfrac{(\mu_i - G_i)}{RT} = \sum x_i\ ln\!\left(\dfrac{\hat{f}_i}{f_i}\right)$

Thus, for an ideal solution, $\dfrac{\Delta G_{mix}}{RT} = \sum x_i\ \dfrac{(\mu_i - G_i)}{RT} = \sum x_i\ ln\!\left(\dfrac{\hat{f}_i}{f_i}\right)$

$\Rightarrow \hat{f}_i^{is} / f_i = x_i \quad \Rightarrow \hat{f}_i^{is} = x_i f_i$

Raoult's Law

$f_i^V = f_i^L \Rightarrow$ Substituting the ideal solution result $\Rightarrow$ $y_i f_i^V = x_i f_i^L$

$\left(f_i^V / P \right) = \varphi(Tr_i, Pr_i, \omega_i)$ for the vapor

We correct the fugacity of the saturated liquid for the effect of pressure on the liquid.

$f_i^{sat} = P_i^{sat} j \left(Tr_i, Pr_i^{sat}, w_i \right)$

$dG = RTd \ln(f) \Rightarrow RT \ln\left(f_i^L / f_i^{sat} \right) = G_i^L - G_i^{sat}$

$(\P G / \P P)_T = (\P H / \P P)_T - T(\P S / \P P)_T = V - T(\P V / \P T)_p + T(\P V / \P T)_p = \underline{V}$

$\Rightarrow \left(G_i^L - G_i^{sat} \right) = \int V^L dP \approx V^L \left(P - P_i^{sat} \right) = RT \ln\left(f_i^L / f_i^{sat} \right)$

$\Rightarrow f_i^L / f_i^{sat} = \exp\left[V^L \left(P - P_i^{sat} \right) / RT \right]$ "Poynting Correction"

Substituting, $y_i P \ (Tr_i, Pr_i) \quad x_i P_i^{sat} j \left(Tr_i, Pr_i^{sat} \right) \exp\left[V^L \left(P - P_i^{sat} \right) / RT \right]$

$$K = _i \ x \quad \frac{_i}{P} \left[\frac{\left(_i, P \ ^{sat} \right) \ \left[V \ \left(\ - P_i \ \right) / \ \right]}{j \left(Tr_i, \ _r \right)} \right]$$

Note: at reasonably low pressures,

$j \approx 1$ and $\exp\left[V^L \left(P - P_i^{sat} \right) / RT \right] \approx 1$ $\qquad \Rightarrow \qquad$ $\boxed{K_i = \dfrac{P_i^{sat}}{P}}$ "Raoult's Law"

Classes of VLE calculations

Type	Information_required	Information_computed	Convergence
BP	T,x	P,y	Easiest
DP	T,y	P,x	Not bad
BT	P,x	T,y	difficult
DT	P,y	T,x	difficult
FL	P,T	$x,y,L/F$	Most difficult

Short-cut Estimation of VLE K-ratios and Initial Guesses for VLE

$$K_i = \frac{10^{\left[7/3\left(1+w_i\right)\left(1-1/Tr_i\right)\right]}}{Pr_i}$$

Bubble Point Pressure: $P = \sum_i P = \sum_i P_i^{sat} = \sum_i Pc_i 10^{\left[\frac{7}{3}\left(1+w_i\right)\left(1-1/Tr_i\right)\right]}$

Dew point pressure,: $\sum x_i = 1 = \sum \frac{y_i}{K_i} = \sum \frac{y_i P}{Pc_i 10^{\left[\frac{7}{3}\left(1+w_i\right)\left(1-1/Tr_i\right)\right]}} \Rightarrow \frac{1}{P} = \sum \frac{y_i}{Pc_i 10^{\left[\frac{7}{3}\left(1+w_i\right)\left(1-1/Tr_i\right)\right]}}$

For bubble or dew point temperatures, it is not so straightforward. One guess would be:

$$T = \sum x_i T_i^{sat}$$

$$T = \sum y_i Tc_i T_i^{sat} / \sum y_i Tc_i$$

But these are somewhat cruder guesses than for the pressures.

Example 9.1 Bubble temperature, dew temperature, and flash

A distillation column is to produce overhead and bottoms products having the following compositions:

	z(Overhead)
Propane	0.23
Isobutane	0.67
n-Butane	0.10
Total	1.00

a) Calculate the temperature at which the condenser must operate in order to condense the overhead product completely at 8 bars.
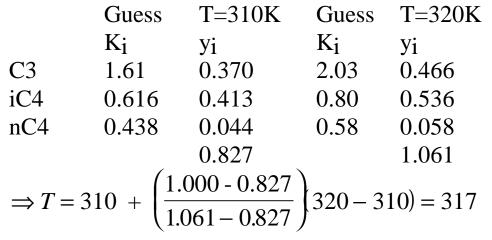
b) Assuming the overhead product vapors are in equilibrium with the liquid on the top plate of the column, calculate the temperature of the overhead vapors and the composition of the liquid on the top plate when operating at the pressure of part (a).

c) Suppose only a partial condensation at 320 K. What fraction of liquid would be condensed?

Example 9.1 Bubble temperature…

Solution: Use the short-cut estimates of the K-ratios
a) The maximum temperature is the bubble point temperature.

	Guess K_i	T=310K y_i	Guess K_i	T=320K y_i
C3	1.61	0.370	2.03	0.466
iC4	0.616	0.413	0.80	0.536
nC4	0.438	0.044	0.58	0.058
		0.827		1.061

$$\Rightarrow T = 310 + \left(\frac{1.000 - 0.827}{1.061 - 0.827} \right)(320 - 310) = 317$$

Example 9.1 Dew temperature…

b) The saturated vapor is at its dew point temperature.

	Guess	T=315K		Guess	T=320K
	y_i	K_i	x_i	K_i	x_i
C3	0.23	1.81	0.127	2.03	0.113
iC4	0.67	0.70	0.957	0.80	0.838
nC4	0.10	0.50	0.200	0.58	0.172
			1.284		1.123

$$\Rightarrow T = 320 + \left(\frac{1.00 - 1.123}{1.281 - 1.123}\right) 320 - 315) = 324$$

Example 9.1 …Flash

c) This is an isothermal flash problem.

M-Bal:

$$z_{C3} = x_{C3} \ (L/F) \ + y_{C3} \ (V/F)$$
$$z_{IC4} = x_{iC4} \ (L/F) \ + y_{iC4} \ (V/F)$$
$$z_{NC4} = x_{nC4} \ (L/F) \ + y_{nC4} \ (V/F)$$

Where z is the feed compostion and L/F is the liquid to feed ratio. Overall, V/F = 1-L/F,

$$z_i = x_i \left[(L/F) + K_i (1 - L/F) \right]$$

$$x_i = \frac{z_i}{K_i + (L/F)(1 - K_i)}$$

$$y_i = \frac{z_i K_i}{K_i + (L/F)(1 - K_i)}$$

Solve $(\Sigma x_i - \Sigma y_i) = 0$. That is

$$\Sigma x - \Sigma y = \Sigma \frac{z_i\left(1 - K_i\right)}{K_i + (L/F)\left(1 - K_i\right)} \equiv \Sigma D_i = 0$$

		Guess	L/F=0.5		L/F=0.6		L/F=0.77
	z_i	K_i	D_i	K_i	D_i	K_i	D_i
C3	0.23	2.03	-0.1564	2.03	-0.1678	2.03	-0.1915
iC4	0.67	0.80	0.1489	0.80	0.1457	0.80	0.1405
nC4	0.10	0.58	0.0532	0.58	0.0505	0.58	0.0465
			0.0457		0.0284		-0.0045

$$\Rightarrow L/F = 0.77 + \left(\frac{0 + 0.0045}{0.0284 + 0.0045}\right)(0.6 - 0.77) = 0.7467$$