Thermodynamics II

Solution Thermodynamics: Theory

Chapter 11

Mixtures and solutions

- Real system usually contains a mixture of fluid.
- Develop the theoretical foundation for applications of thermodynamics to gas mixtures and liquid solutions
- Introducing
  - chemical potential
  - partial properties
  - fugacity
  - excess properties
  - ideal solution

Fundamental property relation

- The basic relation connecting the Gibbs energy to the temperature and pressure in any closed system (Chapter 6):

$$d(nG)=\left[\frac{\partial(nG)}{\partial P}\right]_{T,n}dP+\left[\frac{\partial(nG)}{\partial T}\right]_{P,n}dT=(nV)dP-(nS)dT$$

  - applied to a single-phase fluid in a closed system wherein no chemical reactions occur.

- Consider more general case of single-phase, **open system**:

$$G=G(P,T,n_1,n_2,\ldots,n_i,\ldots n_j,\ldots)$$

$$d(nG)=\left[\frac{\partial(nG)}{\partial P}\right]_{T,n}dP+\left[\frac{\partial(nG)}{\partial T}\right]_{P,n}dT+\sum_i\left[\frac{\partial(nG)}{\partial n_i}\right]_{P,T,n_j}dn_i$$

Define the chemical potential of species i: $$\mu_i \equiv \left[\frac{\partial(nG)}{\partial n_i}\right]_{P,T,n_j}$$

The fundamental property relation for single-phase fluid systems of constant or variable composition:

$$d(nG) = (nV)dP - (nS)dT + \sum_i \mu_i dn_i$$

When the total number of moles of solution is constant (n = constant):

$$dG = VdP - SdT + \sum_i \mu_i dx_i \longrightarrow G = G(P, T, x_1, x_2, \ldots, x_i, \ldots)$$

$$x_i = n_i / n$$

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,x} \qquad S = -\left(\frac{\partial G}{\partial T}\right)_{P,x}$$

The Gibbs energy is expressed as a function of its canonical variables (T, P, and composition.

Solution properties, M

Pure-species properties, M_i

Important remark

When the Gibbs energy is expressed as a function of its canonical variables (T, P, and x), it provides the means for calculation of any thermodynamic property (M) by simple mathematical operations (differentiation and elementary algebra), and implicitly represents complete property information.

Example. Express molar enthalpy, *H*, as function of Gibbs energy G:

$$\boxed{G = H - TS}$$

$$\boxed{H = G + TS} \qquad \boxed{S = -\left(\frac{\partial G}{\partial T}\right)_{P,x}}$$

$$\boxed{H = G - T\left(\frac{\partial G}{\partial T}\right)_{P,x}}$$

Chemical potential and phase equilibria

- Consider a closed system consisting of two phases in equilibrium (T=constant ; P=constant): $\boxed{d(nG)=(nV)dP-(nS)dT=0}$
- Each individual phase is an open system, free to transfer mass to the other:

$$\boxed{d(nG)^{\alpha}=(nV)^{\alpha}dP-(nS)^{\alpha}dT+\sum_i \mu_i^{\alpha}dn_i^{\alpha}} \quad \boxed{d(nG)^{\beta}=(nV)^{\beta}dP-(nS)^{\beta}dT+\sum_i \mu_i^{\beta}dn_i^{\beta}}$$

$$\boxed{nM=(nM)^{\alpha}+(nM)^{\beta}}$$

$$\boxed{d(nG)=(nV)dP-(nS)dT+\sum_i \boxed{\mu_i^{\alpha}dn_i^{\alpha}+\sum_i \mu_i^{\beta}dn_i^{\beta}}=0}$$

Mass balance: $\boxed{n_i=n_i^{\alpha}+n_i^{\beta}}$

$$\boxed{dn_i^{\alpha}=-dn_i^{\beta}} \quad \boxed{n_i\equiv\text{constant}}$$

$$\boxed{\mu_i^{\alpha}=\mu_i^{\beta}\ ;\ i=1,2,\ldots N}$$

Multiple phases at the same T and P are in equilibrium when chemical potential of each species is the same in all phases.

Partial properties

- Define the partial molar property of species *i*:

$$\bar{M}_i \equiv \left[\frac{\partial(nM)}{\partial n_i}\right]_{P,T,n_j}$$

  - the chemical potential and the particle molar Gibbs energy are identical: $\mu_i \equiv \bar{G}_i$
  - for thermodynamic property *M*: $nM = M(P,T,n_1,n_2,\ldots,n_i,\ldots)$

$$\downarrow$$

$$d(nM) = n\left[\frac{\partial M}{\partial P}\right]_{T,n} dP + n\left[\frac{\partial M}{\partial T}\right]_{P,n} dT + \sum_i \bar{M}_i dn_i$$

Solution properties, M
Partial properties, $\bar{M}_i$
Pure-species properties, M_i

$$d(nM) = n\left[\frac{\partial M}{\partial P}\right]_{T,n} dP + n\left[\frac{\partial M}{\partial T}\right]_{P,n} dT + \sum_i \bar{M}_i dn_i$$

$$x_i = n_i / n$$

$$ndM + Mdn = n\left[\frac{\partial M}{\partial P}\right]_{T,n} dP + n\left[\frac{\partial M}{\partial T}\right]_{P,n} dT + \sum_i \bar{M}_i (x_i dn + n dx_i)$$

$$\left[dM - \left(\frac{\partial M}{\partial P}\right)_{T,n} dP - \left(\frac{\partial M}{\partial T}\right)_{P,n} dT - \sum_i \bar{M}_i dx_i\right] n + \left[M - \sum_i x_i \bar{M}_i\right] dn = 0$$

one is free to choose a system of any size, as represented by n, and to choose any variation in its size, as represented by dn. Thus *n* and d*n* are independent and arbitrary:

$$dM - \left(\frac{\partial M}{\partial P}\right)_{T,n} dP - \left(\frac{\partial M}{\partial T}\right)_{P,n} dT - \sum_i \bar{M}_i dx_i = 0$$

and

$$M - \sum_i x_i \bar{M}_i = 0$$

$$M = \sum_i x_i \bar{M}_i$$

Calculation of mixture properties from partial properties

$$dM = \sum_i x_i d\bar{M}_i + \sum_i \bar{M}_i dx_i$$

$$\left(\frac{\partial M}{\partial P}\right)_{T,n} dP + \left(\frac{\partial M}{\partial T}\right)_{P,n} dT - \sum_i x_i d\bar{M}_i = 0$$

The Gibbs/Duhem equation

Partial properties in binary solution

- For binary system

$$\boxed{M = x_1\overline{M}_1 + x_2\overline{M}_2}$$

$$\boxed{dM = \cancel{x_1 d\overline{M}_1} + \overline{M}_1 dx_1 + \cancel{x_2 d\overline{M}_2} + \overline{M}_2 dx_2}$$

$$\boxed{\sum_i x_i d\overline{M}_i = 0}$$

Const. P and T, using Gibbs/Duhem equation

$$\boxed{dM = \overline{M}_1 dx_1 + \overline{M}_2 dx_2}$$

$$\boxed{x_1 + x_2 = 1 \rightarrow dx_2 = -dx_1}$$

$$\boxed{\frac{dM}{dx_1} = \overline{M}_1 - \overline{M}_2}$$

$$\boxed{M = x_1\overline{M}_1 + x_2\overline{M}_2 = x_1\overline{M}_1 + (1-x_1)\overline{M}_2 = x_1(\overline{M}_1 - \overline{M}_2) + \overline{M}_2}$$

$$\boxed{\overline{M}_2 = M - x_1\frac{dM}{dx_1}}$$

Similarly

$$\boxed{\overline{M}_1 = M + x_2\frac{dM}{dx_1}}$$

Example 11.3. The need arises in a laboratory for 2000 cm^3 of an antifreeze solution consisting of 30 mol-% methanol in water. What volumes of pure methanol and of pure water at 25°C must be mixed to form the 2000 cm^3 of antifreeze at 25°C? The partial and pure molar volumes are:

Methanol: $\bar{V}_1 = 38.632\,\text{cm}^3\text{mol}^{-1}$ $\quad V_1 = 40.727\,\text{cm}^3\text{mol}^{-1}$

Water : $\bar{V}_2 = 17.765\,\text{cm}^3\text{mol}^{-1}$ $\quad V_2 = 18.068\,\text{cm}^3\text{mol}^{-1}$

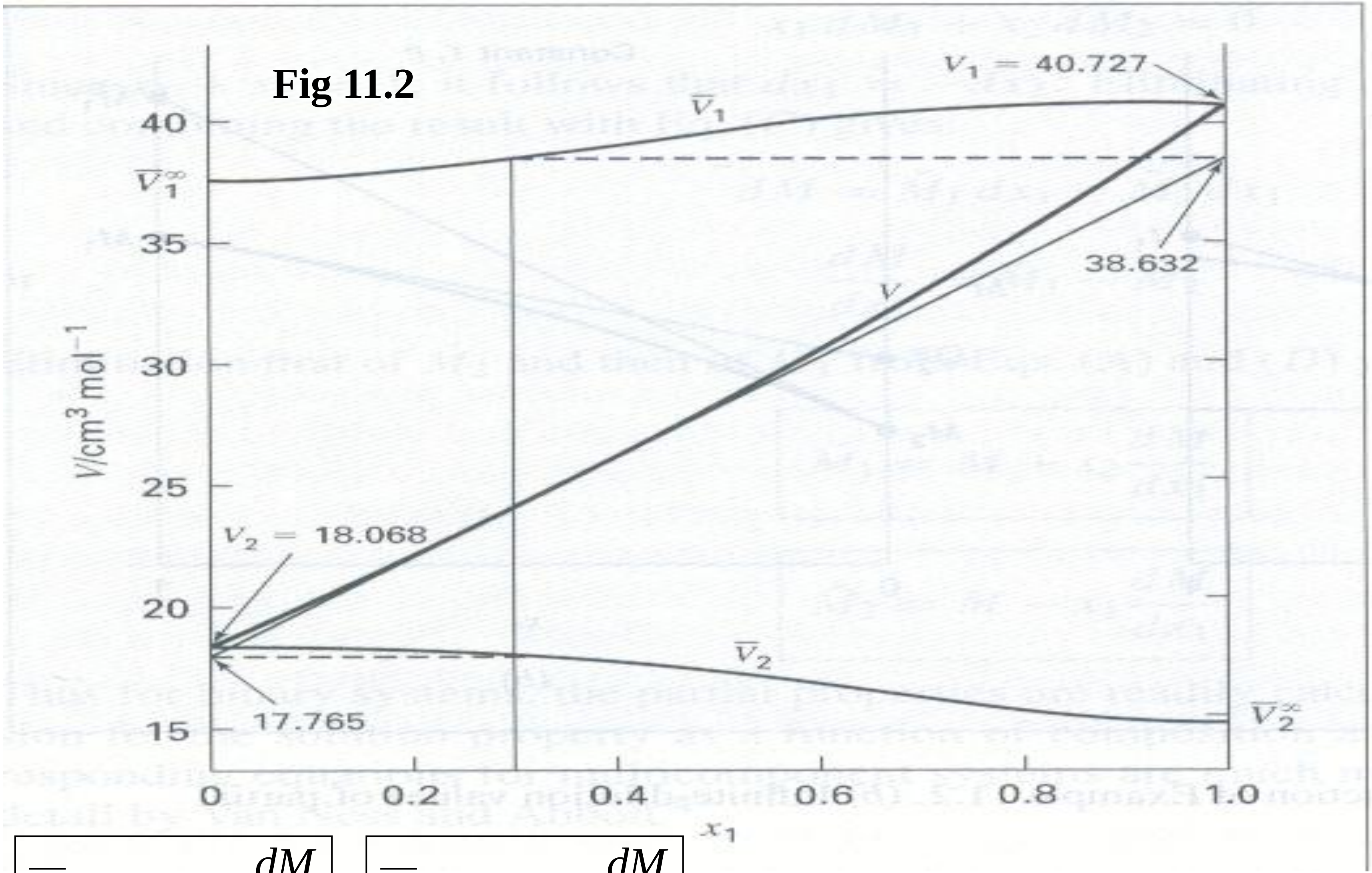
$$\boxed{V = x_1\bar{V}_1 + x_2\bar{V}_2} \longrightarrow \boxed{V = (0.3)(38.632) + (0.7)(17.765) = 24.025\,cm^3/mol}$$

$$\boxed{n = \frac{V^t}{V} = \frac{2000}{24.025} = 83.246\,mol} \longrightarrow \begin{array}{l}\boxed{n_1 = (0.3)(83.246) = 24.974\,mol} \\ \boxed{n_2 = (0.7)(83.246) = 58.272\,mol}\end{array}$$

$$\boxed{V_1^t = n_1 V_1 = (24.974)(40.727) = 1017\,cm^3} \quad \boxed{V_2^t = n_2 V_2 = (58.272)(18.068) = 1053\,cm^3}$$

Fig 11.2 shows how to get the partial molar volumes , if you have solution molar volume as function of composition; $V(x_1)$.

Fig 11.2



$$\bar{M}_2 = M - x_1 \frac{dM}{dx_1}$$

$$\bar{M}_1 = M + x_2 \frac{dM}{dx_1}$$

$$\bar{V}_2 = V - x_1 \frac{dV}{dx_1}$$

$$\bar{V}_1 = V + x_2 \frac{dV}{dx_1}$$

$$\frac{dV}{dx_1} = \text{slope of the tangent line at } x_1$$

Example. The enthalpy of a binary liquid system of species 1 and 2 at fixed T and P is:

$$\boxed{H = 400x_1 + 600x_2 + x_1x_2(40x_1 + 20x_2)}$$

Determine expressions for $\bar{H}_1$ and $\bar{H}_2$ as functions of x_1, numerical values for the pure-species enthalpies H_1 and H_2, and numerical values for the partial enthalpies at infinite dilution $\bar{H}_1^{\infty}$ and $\bar{H}_2^{\infty}$

$$\boxed{x_1 = 1; x_2 = 0:} \quad \boxed{H_1 = 400x_1 + 600x_2 + x_1x_2(40x_1 + 20x_2) = 400}$$

$$\boxed{x_2 = 1; x_1 = 0:} \quad \boxed{H_2 = 400x_1 + 600x_2 + x_1x_2(40x_1 + 20x_2) = 600}$$

$$\boxed{H = 400x_1 + 600x_2 + x_1x_2(40x_1 + 20x_2)}$$

$$\Big\downarrow \ \boxed{x_1 + x_2 = 1}$$

$$\boxed{H = 600 - 180x_1 - 20x_1^3} \xrightarrow{\boxed{x_1 + x_2 = 1}} \boxed{\bar{H}_1 = 420 - 60x_1^2 + 40x_1^3} \quad \boxed{\bar{H}_2 = 600 + 40x_1^3}$$

$$\boxed{\bar{H}_1 = H + x_2\frac{dH}{dx_1}}$$

$$\boxed{\bar{H}_2 = H - x_1\frac{dH}{dx_1}}$$

$$\boxed{x_1 = 0} \ \Big\downarrow \qquad \boxed{x_1 = 1} \ \Big\downarrow$$

$$\boxed{\bar{H}_1^{\infty} = 420\,\frac{J}{mol}} \qquad \boxed{\bar{H}_2^{\infty} = 640\,\frac{J}{mol}}$$

Infinite dilution values of partial enthalpies

Relations among partial properties

$$\boxed{d(nG)=(nV)dP-(nS)dT+\sum_i \bar{G}_i dn_i}$$

- Maxwell relation:

$$\boxed{\left(\frac{\partial V}{\partial T}\right)_{P,n}=-\left(\frac{\partial S}{\partial P}\right)_{T,n}}\quad \boxed{\left(\frac{\partial \bar{G}_i}{\partial T}\right)_{P,n}=-\left[\frac{\partial (nS)}{\partial n_i}\right]_{P,T,n_j}}\quad \boxed{\left(\frac{\partial \bar{G}_i}{\partial P}\right)_{T,n}=\left[\frac{\partial (nV)}{\partial n_i}\right]_{P,T,n_j}}$$

$$\boxed{\left(\frac{\partial \bar{G}_i}{\partial T}\right)_{P,x}=-\bar{S}_i}\qquad \boxed{\left(\frac{\partial \bar{G}_i}{\partial P}\right)_{T,x}=\bar{V}_i}$$

Thus, every equation that provides a *linear relation among thermodynamic* properties of a *constant-composition solution has as its counterpart* an equation connecting the corresponding partial properties of each species in the solution. For example,

$$\boxed{dG=VdP-SdT}\longrightarrow\boxed{d\bar{G}_i=\bar{V}_i dP-\bar{S}_i dT}$$

Relations among partial properties

Example.

$$\boxed{H = U + PV}$$

$$\downarrow$$

$$\boxed{nH = nU + P(nV)}$$

$$\downarrow$$

$$\boxed{\left(\frac{\partial(nH)}{\partial n_i}\right)_{T,P,n_j} = \left(\frac{\partial(nU)}{\partial n_i}\right)_{T,P,n_j} + P\left(\frac{\partial(nV)}{\partial n_i}\right)_{T,P,n_j}}$$

$$\downarrow$$

$$\boxed{\overline{H}_i = \overline{U}_i + P\overline{V}_i}$$

Ideal-gas mixture

$$\bar{V}_i^{ig} = \left[\frac{\partial (nV^{ig})}{\partial n_i} \right]_{P,T,n_j}$$

$$V^{ig} = \frac{RT}{P}$$

$$\bar{V}_i^{ig} = \left[\frac{\partial (n\,RT/P)}{\partial n_i} \right]_{P,T,n_j} = \frac{RT}{P} \left[\frac{\partial (n)}{\partial n_i} \right]_{P,T,n_j}$$

$$n = n_1 + n_1 + \ldots + n_i + \ldots + n_N \rightarrow \left[\frac{\partial (n)}{\partial n_i} \right]_{P,T,n_j} = 1$$

$$\bar{V}_i^{ig} = \frac{RT}{P}$$

$$\boxed{\bar{V}_i^{ig} = V_i^{ig} = V^{ig} = \frac{RT}{P}}$$

Ideal-gas mixture

- **Partial pressure:**

$$\boxed{p_i = y_i P = \frac{y_i RT}{V^{ig}} \quad (i = 1,2,\ldots,N)}$$

- **Gibbs's theorem:** A partial molar property (other than volume) of a constituent species in an ideal-gas mixture is equal to the corresponding molar property of the species as a pure ideal gas at the mixture temperature but at a pressure equal to its partial pressure in the mixture.

$$\boxed{\bar{M}_i^{ig}(T,P) = M_i^{ig}(T,p_i) \quad ; \quad \bar{M}_i^{ig} \neq \bar{V}_i^{ig}}$$

- Remember that enthalpy and internal of ideal gases are independent of pressure:

$$\boxed{\bar{H}_i^{ig}(T,P) = H_i^{ig}(T,p_i) = H_i^{ig}(T)} \qquad \boxed{\bar{U}_i^{ig}(T,P) = U_i^{ig}(T,p_i) = U_i^{ig}(T)}$$

$$\bar{H}_i^{ig}(T,P) = H_i^{ig}(T,p_i) = H_i^{ig}(T,P) \xrightarrow{M = \sum_i x_i \bar{M}_i} H^{ig} = \sum_i y_i H_i^{ig} \qquad U^{ig} = \sum_i y_i U_i^{ig}$$

From Chapter 6: $dS^{ig} = C_P^{ig}\, dT/T - R\,dP/P \rightarrow dS_i^{ig} = -R\,d\ln P \quad const.T$

$$S_i^{ig}(T,P) - S_i^{ig}(T,p_i) = -R\ln\frac{P}{p_i} = -R\ln\frac{P}{y_i P} = R\ln y_i$$

$$M = \sum_i x_i \bar{M}_i \qquad \bar{M}_i^{ig}(T,P) = M_i^{ig}(T,p_i)$$

$$\downarrow$$

$$S_i^{ig}(T,P) - \bar{S}_i^{ig}(T,P) = R\ln y_i \longrightarrow S^{ig} = \sum_i y_i S_i^{ig} - R\sum_i y_i \ln y_i$$

$$\bar{G}_i^{ig} = \bar{H}_i^{ig} - T\bar{S}_i^{ig} \xrightarrow[S_i^{ig}(T,P) - \bar{S}_i^{ig}(T,P) = -R\ln y_i]{\bar{H}_i^{ig}(T,P) = H_i^{ig}(T,P)} \bar{G}_i^{ig} = H_i^{ig} - TS_i^{ig} + RT\ln y_i$$

$$\downarrow$$

$$\mu_i^{ig} \equiv \bar{G}_i^{ig} = G_i^{ig} + RT\ln y_i$$

or

$$G_i^{ig} = \Gamma_i(T) + RT\ln P$$

From integration of at const T

$$dG_i^{ig} = V_i^{ig}\,dP = \frac{RT}{P}\,dP = RT\,d\ln P$$

$$\mu_i^{ig} = \Gamma_i(T) + RT\ln y_i P$$

$$\downarrow$$

$$G^{ig} = \sum_i y_i \Gamma_i(T) + RT\sum_i y_i \ln y_i P$$

$\Gamma_i(T)$: Integration const; f(T)

Fugacity and fugacity coefficient of pure species

- Chemical potential: $$\boxed{\mu_i \equiv \left[\frac{\partial(nG)}{\partial n_i}\right]_{P,T,n_j}}$$
    - provides fundamental criterion for phase equilibria
    - however, the Gibbs energy, hence μ_i, is defined in relation to the internal energy and entropy - (absolute values are unknown).
- Ideal gas: $$\boxed{G_i^{ig} = \Gamma_i(T) + RT \ln P}$$
- Real pure gas or pure liquid; fugacity is defined:

$$\boxed{G_i \equiv \Gamma_i(T) + RT \ln f_i}$$

   - a quantity that takes the place of P

With units of pressure

Fugacity and fugacity coefficient

$$\boxed{G_i \equiv \Gamma_i(T) + RT \ln f_i}$$

$$\boxed{G_i^{ig} = \Gamma_i(T) + RT \ln P}$$

$$\boxed{G_i - G_i^{ig} = RT \ln \frac{f_i}{P}} \longrightarrow \boxed{G_i^R = RT \ln \phi_i}$$

Residual Gibbs energy

Fugacity coefficient

$$\boxed{\phi_i = \frac{f_i}{P}}$$

From chapter 6 $\boxed{\dfrac{G^R}{RT} = \int_0^P (Z-1)\dfrac{dP}{P}}$

$$\boxed{\ln \phi_i = \int_0^P (Z_i - 1)\frac{dP}{P} \qquad (const.\, T)}$$

Fugacity coefficient from Generic EOS

Fugacity coefficient of pure species through cubic EOS as van der Waals, Redlich/Kwong, Soave/Redlich/Kwong, and Peng/Robinson:

$$\boxed{\ln \phi_i = Z_i - 1 - \ln(Z_i - \beta_i) - q_i I_i}$$

$$\boxed{\beta \equiv \frac{bP}{RT} = \Omega \frac{P_r}{T_r}} \quad \boxed{q \equiv \frac{a(T)}{bRT} = \frac{\Psi \alpha(T_r)}{\Omega T_r}}$$

See Table 3.1 to get the parameters

Vapor & Vapor-Like:

$$\boxed{Z = 1 + \beta - q\beta \frac{Z - \beta}{(Z + \epsilon\beta)(Z + \sigma\beta)}}$$

start with Z=1 and then iterate

(Chapter 3)

Liquid & Liquid-Like:

$$\boxed{Z = \beta + (Z + \epsilon\beta)(Z + \sigma\beta)\left(\frac{1 + \beta - Z}{q\beta}\right)}$$

start with Z=β and then iterate

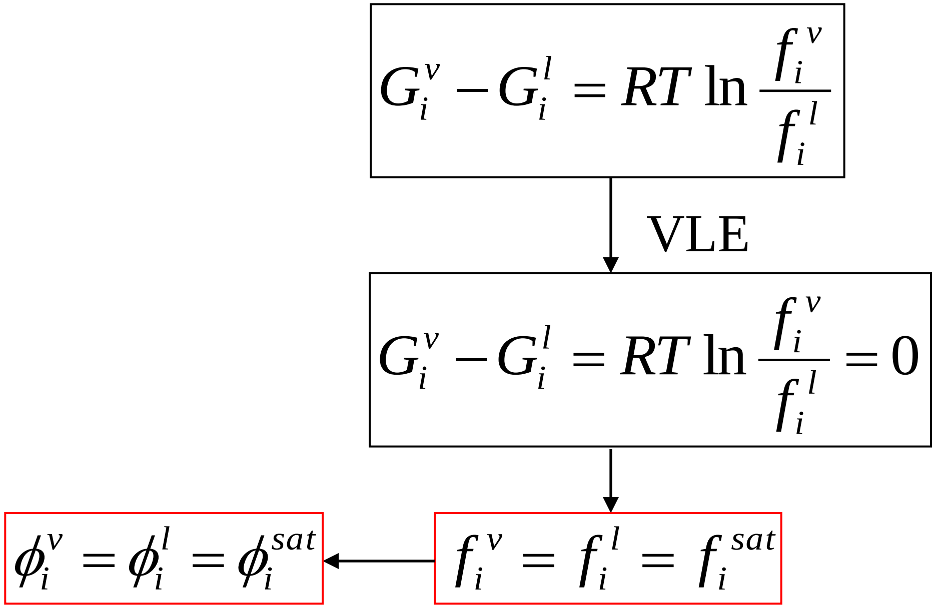
$$\boxed{I = \frac{\beta}{Z} = \quad vdw, const\ T}$$

$$\boxed{I \equiv \frac{1}{\sigma - \epsilon} \ln\left(\frac{Z + \sigma\beta}{Z + \epsilon\beta}\right) \quad RK, SRK, PR\ at\ const\ T}$$

(Chapter 6)

VLE for pure species

- Saturated vapor: $\boxed{G_i^v = \Gamma_i(T) + RT \ln f_i^{\,v}}$
- Saturated liquid: $\boxed{G_i^l = \Gamma_i(T) + RT \ln f_i^{\,l}}$



$$\boxed{G_i^v - G_i^l = RT \ln \frac{f_i^{\,v}}{f_i^{\,l}}}$$

$$\Big\downarrow \text{VLE}$$

$$\boxed{G_i^v - G_i^l = RT \ln \frac{f_i^{\,v}}{f_i^{\,l}} = 0}$$

$$\Big\downarrow$$

$$\boxed{\phi_i^v = \phi_i^l = \phi_i^{sat}} \longleftarrow \boxed{f_i^{\,v} = f_i^{\,l} = f_i^{\,sat}}$$

For a pure species coexisting liquid and vapor phases are in equilibrium when they have the same temperature, pressure, fugacity and fugacity coefficient.

Fugacity of a pure liquid

- The fugacity of pure species *i* as a compressed liquid:

$$\boxed{G_i - G_i^{sat} = RT \ln \frac{f_i}{f_i^{sat}}}$$

$$\boxed{dG_i = V_i dP - S_i dT}$$

$$\boxed{G_i - G_i^{sat} = \int_{P_i^{sat}}^{P} V_i dP \quad (isothermal\ \ process)}$$

$$\boxed{\ln \frac{f_i}{f_i^{sat}} = \frac{1}{RT} \int_{P_i^{sat}}^{P} V_i dP}$$

Since V_i is a weak function of P

$$\boxed{\ln \frac{f_i}{f_i^{sat}} = \frac{V_i^l (P - P_i^{sat})}{RT}}$$

$$\boxed{f_i^{sat} = \phi_i^{sat} P_i^{sat}}$$

$$\boxed{f_i = \phi_i^{sat} P_i^{sat} \exp \frac{V_i^l (P - P_i^{sat})}{RT}}$$

Example 11.5. For H_2O at a temperature of 300°C and for pressures up to 10,000 kPa (100 bar) calculate values of f_i and φ_i from data in the steam tables and plot them vs. P.

For a state at P: $\boxed{G_i = \Gamma_i(T) + RT \ln f_i}$

For a low pressure (ideal gas) reference state: $\boxed{G_i^{ig} = \Gamma_i(T) + RT \ln P}$

$$\boxed{\ln \frac{f_i}{P} = \frac{1}{R}\left[\frac{H_i - H_i^{ig}}{T} - (S_i - S_i^{ig})\right]} \longleftarrow \boxed{\ln \frac{f_i}{P} = \frac{1}{RT}(G_i - G_i^{ig})}$$

$$\boxed{G_i = H_i - TS_i}$$

$$\boxed{G_i^{ig} = H_i^{ig} - TS_i^{ig}}$$

$$\boxed{\phi_i = f_i / P}$$

The low pressure (say 1 kPa) at 300°C (Ideal superheated vapor):

From steam tables: $\boxed{S_i^{ig} = 10.3450\, J/gK}$ $\boxed{H_i^{ig} = 3076.8\, J/g}$

Vapor state(P ≤ P^{sat} = 8592.7 kPa):

Get values of S_i and H_i from steam tables. Then calculate values of f_i and ϕ_i.

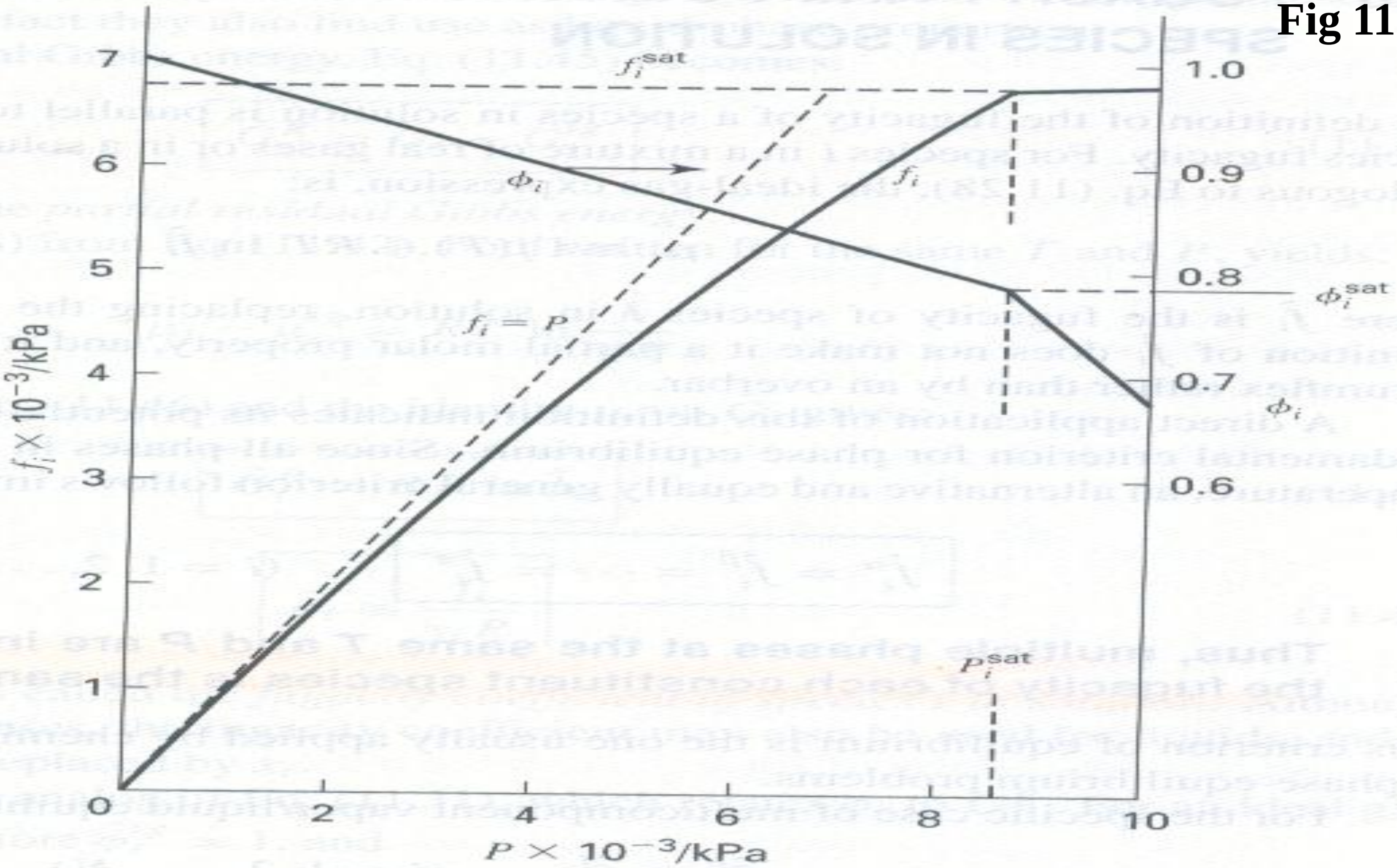
Subcooled state (10000kPa ≥ P > P^{sat}):

Values of f_i and φ_i for subcooled water (10000kPa ≥ P > P^{sat} =8592.7) :

$$\boxed{f_i = \phi_i^{sat} P_i^{sat} \exp \frac{V_i^l (P - P_i^{sat})}{RT}} \qquad \phi_i^{sat} = \phi_i^v = \phi_i^l$$

Example 11.5:

Fig 11.3



Exercise . Resolve Example 11.5 using van der Waal EOS to obtain the above figure.

Fugacity and fugacity coefficient: species in real gas mixture or liquid solution

- For species *i* in a mixture of real gases or in a solution of liquids:

$$\boxed{\mu_i \equiv \Gamma_i(T) + RT\ln \hat{f}_i}$$

Fugacity of species *i* in solution (replacing the partial pressure)

- Multiple phases at the same T and P are in equilibrium when the fugacity of each constituent species is the same in all phases:

$$\boxed{\hat{f}_i^{\alpha} = \hat{f}_i^{\beta} = \dots = \hat{f}_i^{\pi}}$$

The residual property: $\boxed{M^R = M - M^{ig}}$

The partial residual property: $\boxed{\bar{M}_i^R = \bar{M}_i - \bar{M}_i^{ig}}$

$$\boxed{\bar{G}_i^R = \bar{G}_i - \bar{G}_i^{ig}}$$

$$\boxed{\mu_i \equiv \Gamma_i(T) + RT \ln \hat{f}_i}$$

$$\boxed{\mu_i^{ig} = \Gamma_i(T) + RT \ln y_i P}$$

$$\boxed{\mu_i - \mu_i^{ig} = RT \ln \frac{\hat{f}_i}{y_i P}}$$

$$\boxed{\mu_i \equiv \left[\frac{\partial(nG)}{\partial n_i}\right]_{P,T,n_j} = \bar{G}_i}$$

$$\boxed{\bar{G}_i^R = RT \ln \hat{\phi}_i}$$

$$\boxed{\hat{\phi}_i \equiv \frac{\hat{f}_i}{y_i P}}$$

The fugacity coefficient of species *i* in solution

For ideal gas,

$$\boxed{\bar{G}_i^R = 0}$$

$$\boxed{\hat{\phi}_i = \frac{\hat{f}_i}{y_i P} = 1} \longrightarrow \boxed{\hat{f}_i = y_i P}$$

Fundamental residual-property relation

$$d\left(\frac{nG}{RT}\right)=\frac{1}{RT}d(nG)-\frac{nG}{RT^2}dT$$

$$d(nG)=(nV)dP-(nS)dT+\sum_i \mu_i dn_i$$

$$G=H-TS$$

$$d\left(\frac{nG}{RT}\right)=\frac{nV}{RT}dP-\frac{nH}{RT^2}dT+\sum_i\frac{\bar{G}_i}{RT}dn_i \longrightarrow \frac{nG}{RT}=f(P,T,n_i)$$

G/RT as a function of its canonical variables allows evaluation of all other thermodynamic properties, and implicitly contains complete property information.

The residual properties:

$$d\left(\frac{nG^R}{RT}\right)=\frac{nV^R}{RT}dP-\frac{nH^R}{RT^2}dT+\sum_i\frac{\bar{G}_i^R}{RT}dn_i$$

$$\bar{G}_i^R=RT\ln\hat{\phi}_i$$

$$d\left(\frac{nG^R}{RT}\right)=\frac{nV^R}{RT}dP-\frac{nH^R}{RT^2}dT+\sum_i\ln\hat{\phi}_i dn_i$$

Fundamental residual-property relation

$$\boxed{d\left(\frac{nG^R}{RT}\right) = \frac{nV^R}{RT}dP - \frac{nH^R}{RT^2}dT + \sum_i \frac{\overline{G}_i^R}{RT}dn_i}$$

$$\boxed{d\left(\frac{nG^R}{RT}\right) = \frac{nV^R}{RT}dP - \frac{nH^R}{RT^2}dT + \sum_i \ln\hat{\phi}_i dn_i}$$

Fix T and composition: $\longrightarrow$ $\boxed{\frac{V^R}{RT} = \left(\frac{\partial(G^R/RT)}{\partial P}\right)_{T,x}}$

Fix P and composition: $\longrightarrow$ $\boxed{\frac{H^R}{RT} = -T\left(\frac{\partial(G^R/RT)}{\partial T}\right)_{P,x}}$

Fix T and P: $\longrightarrow$ $\boxed{\ln\hat{\phi}_i = \left(\frac{\partial(nG^R/RT)}{\partial n_i}\right)_{P,T,n_j}}$

From Chapter 6: $\boxed{\frac{G^R}{RT} = \int_0^P (Z-1)\frac{dP}{P}}$

Example 11.6. Develop a general equation for calculation of $\ln \hat{\phi}_i$ values form compressibility-factor data.

$$\boxed{\ln \hat{\phi}_i = \left(\frac{\partial (nG^R / RT)}{\partial n_i} \right)_{P,T,n_j}}$$

$$\boxed{\frac{nG^R}{RT} = \int_0^P (nZ - n) \frac{dP}{P}}$$

$$\boxed{\ln \hat{\phi}_i = \int_0^P \left[\frac{\partial (nZ - n)}{\partial n_i} \right]_{P,T,n_j} \frac{dP}{P}}$$

$$\boxed{\frac{\partial n}{\partial n_i} = 1} \qquad \boxed{\frac{\partial (nZ)}{\partial n_i} = \bar{Z}_i}$$

$$\boxed{\ln \hat{\phi}_i = \int_0^P (\bar{Z}_i - 1) \frac{dP}{P}}$$

Integration at constant temperature and composition

Fugacity coefficient from the virial EOS

- The virial equation: $\boxed{Z = 1 + \frac{BP}{RT}}$
  - The mixture second virial coefficient B: $\boxed{B = \sum_i \sum_j y_i y_j B_{ij}}$
  - For a binary mixture: $\boxed{B = y_1 y_1 B_{11} + y_1 y_2 B_{12} + y_2 y_1 B_{21} + y_2 y_2 B_{22}}$

$$\boxed{B_{ij} = B_{ji}}$$

$\underset{i=j}{B_{ij}}$: Pure species virial coefficient

$\underset{i\neq j}{B_{ij}}$: Cross virial coefficient

- For *n* moles of gas mixture:

$$\boxed{nZ = n + \frac{nBP}{RT}} \longrightarrow \boxed{\bar{Z}_1 = \left[\frac{\partial (nZ)}{\partial n_1}\right]_{P,T,n_2} = 1 + \frac{P}{RT}\left[\frac{\partial (nB)}{\partial n_1}\right]_{T,n_2}}$$

$$\boxed{\ln \hat{\phi}_i = \int_0^P (\bar{Z}_i - 1)\frac{dP}{P}}$$

$$\downarrow$$

$$\boxed{\ln \hat{\phi}_1 = \frac{1}{RT}\int_0^P \left[\frac{\partial (nB)}{\partial n_1}\right]_{T,n_2} dP = \frac{P}{RT}\left[\frac{\partial (nB)}{\partial n_1}\right]_{T,n_2}}$$

Fugacity coefficient from the virial EOS

$$\ln\hat{\phi}_1 = \frac{1}{RT}\int_0^P \left[\frac{\partial(nB)}{\partial n_1}\right]_{T,n_2} dP = \frac{P}{RT}\left[\frac{\partial(nB)}{\partial n_1}\right]_{T,n_2}$$

$$B = y_1 y_1 B_{11} + y_1 y_2 B_{12} + y_2 y_1 B_{21} + y_2 y_2 B_{22}$$

$$\delta_{12} \equiv 2B_{12} - B_{11} - B_{22}$$

$$y_i = n_i / n$$

$$\ln\hat{\phi}_1 = \frac{P}{RT}\left(B_{11} + y_2^2\delta_{12}\right)$$

Similarly: $\ln\hat{\phi}_2 = \frac{P}{RT}\left(B_{22} + y_1^2\delta_{12}\right)$

For multicomponent gas mixture, the general form:

$$\ln\hat{\phi}_k = \frac{P}{RT}\left(B_{kk} + \frac{1}{2}\sum_i\sum_j y_i y_j (2\delta_{ik} - \delta_{ij})\right)$$

where $\delta_{ik} \equiv 2B_{ik} - B_{ii} - B_{kk}$

Example 11.7. Determine the fugacity coefficients for nitrogen and methane in $N_2(1)/CH_4(2)$ mixture at 200K and 30 bar if the mixture contains 40 mol-% N_2. Experimental virial-coefficients are:

$$\boxed{B_{11} = -35.2 \quad B_{22} = -105.0 \quad B_{12} = -59.8 \quad cm^3/mol}$$

$$\boxed{\delta_{12} \equiv 2B_{12} - B_{11} - B_{22} = 2(-59.8) + 35.2 + 105.0 = 20.6\, cm^3/mol}$$

$$\boxed{\ln \hat{\phi}_1 = \frac{P}{RT}\left(B_{11} + y_2^2 \delta_{12}\right) = \frac{30}{(83.14)(200)}\left[-35.2 + (0.6)^2(20.6)\right] = -0.0501}$$

$$\downarrow$$

$$\boxed{\hat{\phi}_1 = 0.9511}$$

$$\boxed{\ln \hat{\phi}_2 = \frac{P}{RT}\left(B_{22} + y_1^2 \delta_{12}\right) = \frac{30}{(83.14)(200)}\left[-105.0 + (0.4)^2(20.6)\right] = -0.1835}$$

$$\downarrow$$

$$\boxed{\hat{\phi}_2 = 0.8324}$$

Generalized correlations for the fugacity coefficient

Pure gas:

$$\ln \phi_i = \int_0^{P_r} (Z_i - 1)\frac{dP_r}{P_r} \qquad (const.\, T_r)$$

$$Z - 1 = \frac{P_r}{T_r}(B^0 + \omega B^1)$$

Pitzer correlations

$$\ln \phi = \frac{P_r}{T_r}(B^0 + \omega B^1)$$

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}}$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

Lee/Kesler correlation

$$Z = Z^0 + \omega Z^1$$

$$\ln \phi = \int_0^{P_r} (Z^0 - 1)\frac{dP_r}{P_r} + \omega \int_0^{P_r} Z^1 \frac{dP_r}{P_r} \qquad (const.\, T_r)$$

$$\ln \phi^0 \equiv \int_0^{P_r} (Z^0 - 1)\frac{dP_r}{P_r}$$

$$\ln \phi^1 \equiv \int_0^{P_r} Z^1 \frac{dP_r}{P_r}$$

$$\ln \phi = \ln \phi^0 + \omega \ln \phi^1$$ or $$\phi = (\phi^0)(\phi^1)^{\omega}$$

Get ϕ^0 and ϕ^1 from Tables E13:E16 in Appendix E

Generalized correlations for the fugacity coefficient

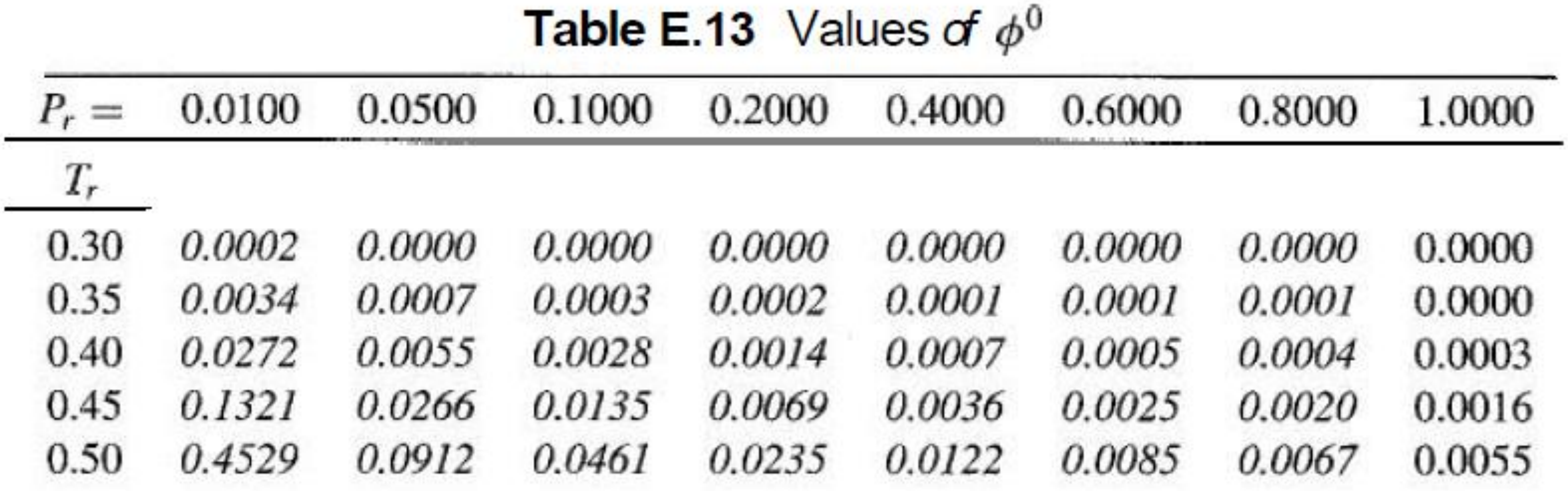


Table E.13 Values of ϕ^0

$P_r =$ T_r	0.0100	0.0500	0.1000	0.2000	0.4000	0.6000	0.8000	1.0000
0.30	0.0002	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.35	0.0034	0.0007	0.0003	0.0002	0.0001	0.0001	0.0001	0.0000
0.40	0.0272	0.0055	0.0028	0.0014	0.0007	0.0005	0.0004	0.0003
0.45	0.1321	0.0266	0.0135	0.0069	0.0036	0.0025	0.0020	0.0016
0.50	0.4529	0.0912	0.0461	0.0235	0.0122	0.0085	0.0067	0.0055

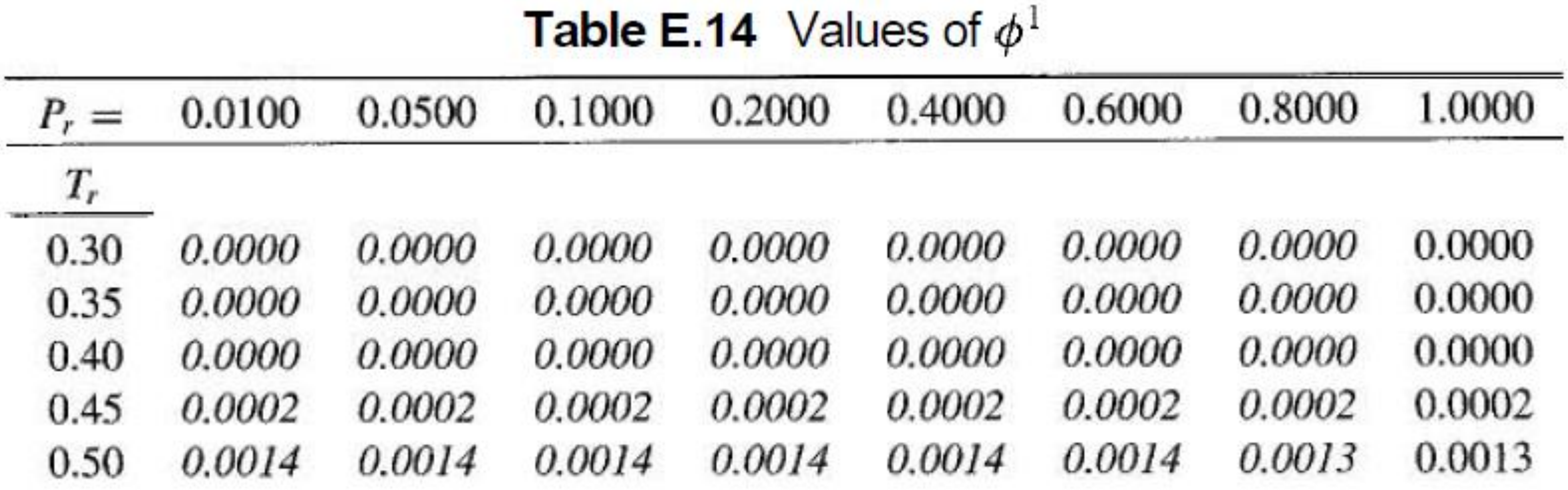


Table E.14 Values of ϕ^1

$P_r =$ T_r	0.0100	0.0500	0.1000	0.2000	0.4000	0.6000	0.8000	1.0000
0.30	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.35	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.40	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.45	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002
0.50	0.0014	0.0014	0.0014	0.0014	0.0014	0.0014	0.0013	0.0013

See Appendix E, Tables E13 ~ E16 for higher Tr

Generalized correlations for the fugacity coefficient

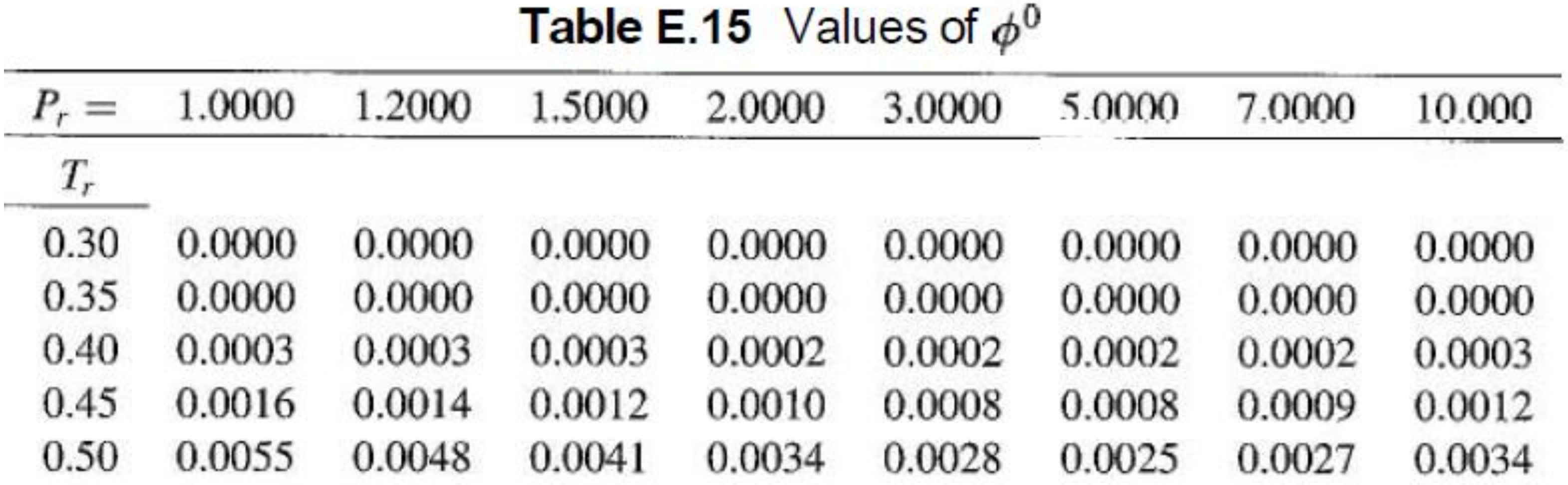


Table E.15 Values of ϕ^0

$P_r =$ T_r	1.0000	1.2000	1.5000	2.0000	3.0000	5.0000	7.0000	10.000
0.30	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.35	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.40	0.0003	0.0003	0.0003	0.0002	0.0002	0.0002	0.0002	0.0003
0.45	0.0016	0.0014	0.0012	0.0010	0.0008	0.0008	0.0009	0.0012
0.50	0.0055	0.0048	0.0041	0.0034	0.0028	0.0025	0.0027	0.0034

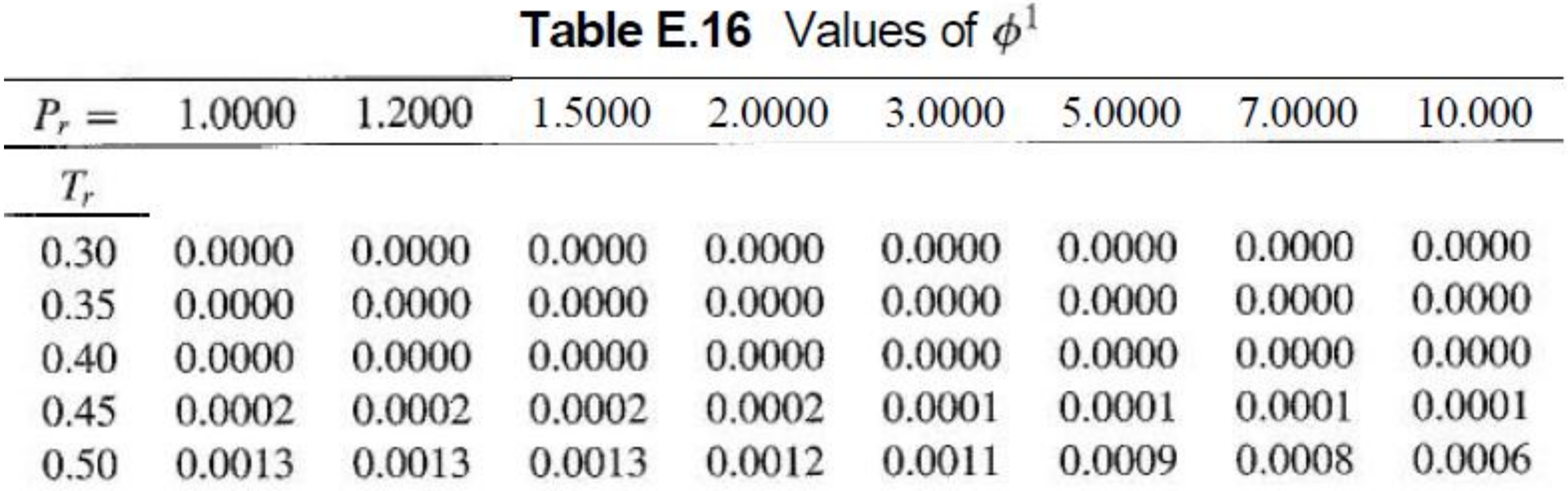


Table E.16 Values of ϕ^1

$P_r =$ T_r	1.0000	1.2000	1.5000	2.0000	3.0000	5.0000	7.0000	10.000
0.30	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.35	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.40	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.45	0.0002	0.0002	0.0002	0.0002	0.0001	0.0001	0.0001	0.0001
0.50	0.0013	0.0013	0.0013	0.0012	0.0011	0.0009	0.0008	0.0006

See Appendix E, Tables E13 ~ E16 for higher Tr

Example 11.8. Estimate a value for the fugacity of 1-butene vapor at 200°C and 70 bar.

$$\left.\begin{array}{l}\boxed{T_r = 1.127}\\ \\ \boxed{P_r = 1.731}\\ \\ \boxed{\omega = 0.191}\end{array}\right\} \quad \boxed{\phi^0 = 0.627} \qquad \text{and} \qquad \boxed{\phi^1 = 1.096}$$

Table E15 and E16

$$\boxed{\ln\phi = \ln\phi^0 + \omega\ln\phi^1} \longrightarrow \boxed{\phi = 0.638} \longrightarrow \boxed{f = \phi P = (0.638)(70) = 44.7\ bar}$$

Generalized correlations for the fugacity coefficient

Extension to gas mixtures:

$$\ln \hat{\phi}_k = \frac{P}{RT}\left(B_{kk} + \frac{1}{2}\sum_i \sum_j y_i y_j (2\delta_{ik} - \delta_{ij})\right)$$

Pitzer correlations

$$\delta_{ik} \equiv 2B_{ik} - B_{ii} - B_{kk}$$

$$B_{ij} = \frac{RT_{cij}}{P_{cij}}(B^0 + \omega_{ij} B^1)$$

$$\omega_{ij} = \frac{\omega_i + \omega_j}{2}$$

Empirical interaction parameter

$$T_{cij} = \sqrt{(T_{ci} T_{cj})}(1 - k_{ij})$$

Prausnitz et al. 1986

$$T_{rij} = \frac{T}{T_{cij}}$$

$$P_{cij} = \frac{Z_{cij} RT_{cij}}{V_{cij}}$$

$$Z_{cij} = \frac{Z_{ci} + Z_{cj}}{2}$$

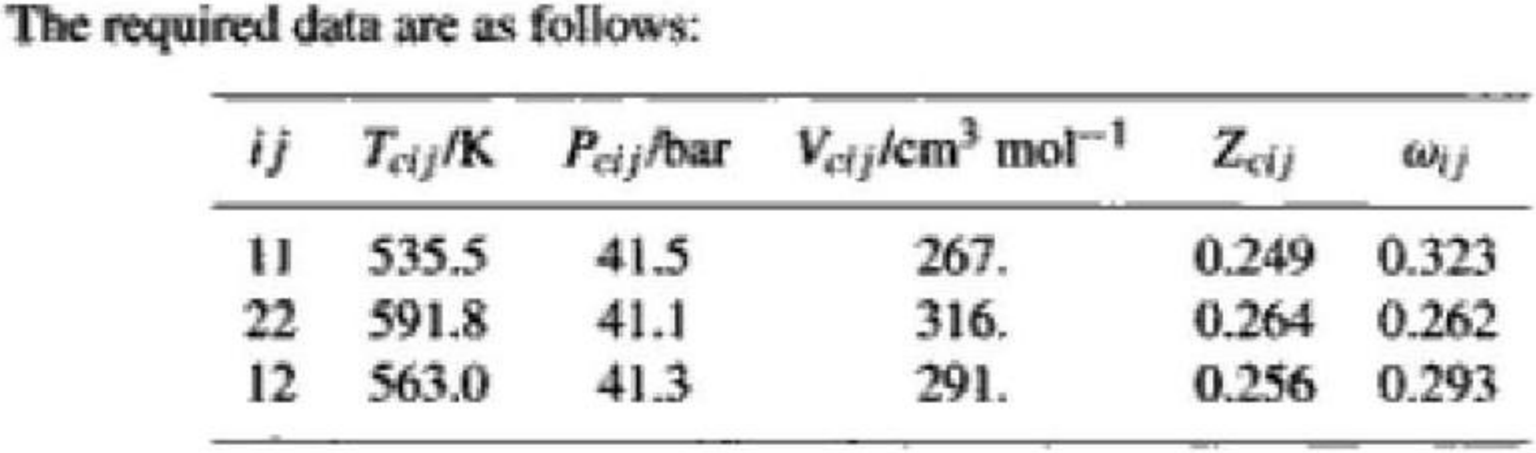
$$V_{cij} = \left(\frac{V_{ci}^{1/3} + V_{cj}^{1/3}}{2}\right)^3$$

$$B^0 = 0.083 - \frac{0.422}{T_{rij}^{1.6}}$$

$$B^1 = 0.139 - \frac{0.172}{T_{rij}^{4.2}}$$

(Chapter 3)

Example 11.9 Estimate $\hat{\phi}_1$ and $\hat{\phi}_2$ for an equimolar mixture of methyl ethyl ketone (1) / toluene (2) at 50°C and 25 kPa. Set all $k_{ij} = 0$.



The required data are as follows:

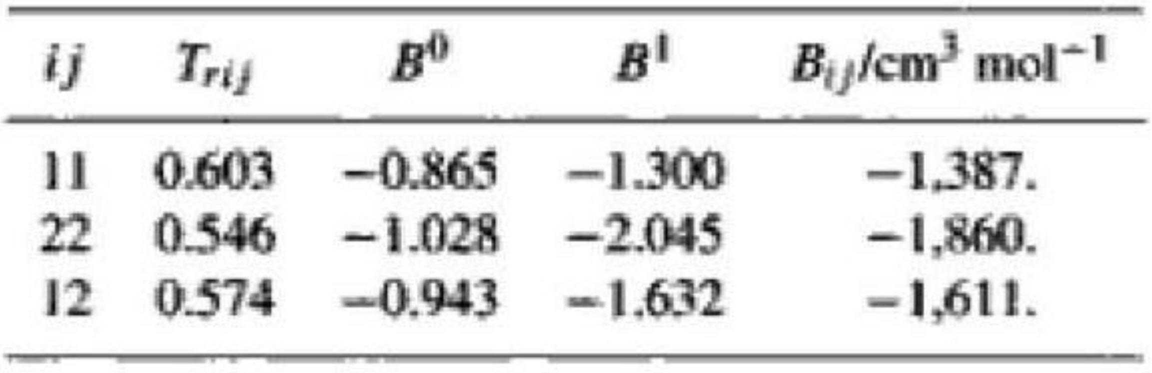
ij	T_{cij}/K	P_{cij}/bar	V_{cij}/cm^3 mol^{-1}	Z_{cij}	ω_{ij}
11	535.5	41.5	267.	0.249	0.323
22	591.8	41.1	316.	0.264	0.262
12	563.0	41.3	291.	0.256	0.293

$$\boxed{\omega_{ij} = \frac{\omega_i + \omega_j}{2}} \qquad \boxed{Z_{cij} = \frac{Z_{ci} + Z_{cj}}{2}} \qquad \boxed{P_{cij} = \frac{Z_{cij} R T_{cij}}{V_{cij}}} \qquad \boxed{T_{cij} = \sqrt{(T_{ci} T_{cj})}(1 - k_{ij})}$$

$$\boxed{T_{rij} = \frac{T}{T_{cij}}} \qquad \boxed{B^0 = 0.083 - \frac{0.422}{T_{rij}^{1.6}}} \qquad \boxed{B^1 = 0.139 - \frac{0.172}{T_{rij}^{4.2}}}$$

$$\boxed{B_{ij} = \frac{R T_{cij}}{P_{cij}} (B^0 + \omega_{ij} B^1)}$$

Example 11.9 Estimate $\hat{\phi}_1$ and $\hat{\phi}_2$ for an equimolar mixture of methyl ethyl ketone (1) / toluene (2) at 50°C and 25 kPa. Set all $k_{ij} = 0$.



ij	$T_{r_{ij}}$	B^0	B^1	B_{ij}/cm^3 mol^{-1}
11	0.603	−0.865	−1.300	−1,387.
22	0.546	−1.028	−2.045	−1,860.
12	0.574	−0.943	−1.632	−1,611.

$$\boxed{\delta_{12} \equiv 2B_{12} - B_{11} - B_{22} = 25\, cm^3/mol}$$

$$\boxed{\ln \hat{\phi}_1 = \frac{P}{RT}\left(B_{11} + y_2^2\delta_{12}\right) = -0.0128} \longrightarrow \boxed{\hat{\phi}_1 = 0.987}$$

$$\boxed{\ln \hat{\phi}_2 = \frac{P}{RT}\left(B_{22} + y_1^2\delta_{12}\right) = -0.0172} \longrightarrow \boxed{\hat{\phi}_2 = 0.983}$$

The ideal solution

- Ideal gas mixture: $\boxed{\bar{G}_i^{ig} = G_i^{ig} + RT\ln y_i}$
- In analogy, ideal solution is defined such that: $\boxed{\bar{G}_i^{id} = G_i + RT\ln x_i}$

$$\boxed{\bar{G}_i^{id} = G_i + RT\ln x_i} \xrightarrow{\boxed{M^{id} = \sum_i x_i \bar{M}_i^{id}}} \boxed{G^{id} = \sum_i x_i G_i + RT\sum_i x_i \ln x_i}$$

$$\boxed{\bar{S}_i^{id} = -\left(\frac{\partial \bar{G}_i^{id}}{\partial T}\right)_{P,x} = -\left(\frac{\partial G_i}{\partial T}\right)_P - R\ln x_i} \longrightarrow \boxed{\bar{S}_i^{id} = S_i - R\ln x_i} \boxed{S^{id} = \sum_i x_i S_i - R\sum_i x_i \ln x_i}$$

$$\boxed{\bar{V}_i^{id} = -\left(\frac{\partial \bar{G}_i^{id}}{\partial P}\right)_{T,x} = -\left(\frac{\partial G_i}{\partial P}\right)_T} \longrightarrow \boxed{\bar{V}_i^{id} = V_i} \boxed{V^{id} = \sum_i x_i V_i}$$

$$\boxed{\bar{H}_i^{id} = \bar{G}_i^{id} + T\bar{S}_i^{id} = G_i + RT\ln x_i + TS_i - RT\ln x_i} \longrightarrow \boxed{\bar{H}_i^{id} = H_i} \boxed{H^{id} = \sum_i x_i H_i}$$

The Lewis/Randall Rule

- For species i in gas or liquid mixture: $\boxed{\mu_i = \overline{G}_i = \Gamma_i(T) + RT \ln \hat{f}_i}$
- For pure species i (gas or liquid): $\boxed{G_i \equiv \Gamma_i(T) + RT \ln f_i}$
- Subtraction gives: $\boxed{\mu_i = \overline{G}_i = G_i + RT \ln\left(\hat{f}_i / f_i\right)}$
- For species *i* in an ideal solution: $\boxed{\mu_i^{id} = \overline{G}_i^{id} = G_i + RT \ln\left(\hat{f}_i^{id} / f_i\right)}$
- Ideal solution: $\boxed{\mu_i^{id} = \overline{G}_i^{id} = G_i + RT \ln x_i}$
- Compare to have the **Lewis/Randall rule**: $\boxed{\hat{f}_i^{id} = x_i f_i}$

$$\boxed{f_i = \phi_i P} \qquad \boxed{\hat{f}_i^{id} = y_i P \hat{\phi}_i^{id} = x_i P \hat{\phi}_i^{id}}$$

$$\boxed{\hat{\phi}_i^{id} = \phi_i}$$

The fugacity coefficient of species *i* in an ideal solution is equal to the fugacity coefficient of pure species *i* in the same physical state as the solution and at the same *T* and *P*.

Excess properties

- The mathematical formalism of excess properties is analogous to that of the residual properties:

$$\boxed{M^E \equiv M - M^{id}}$$

  - where M represents the molar (or unit-mass) value of any extensive thermodynamic property (e.g., V, U, H, S, G, etc.)
  - Similarly to residual properties:

$$\boxed{d\left(\frac{nG^E}{RT}\right) = \frac{nV^E}{RT}dP - \frac{nH^E}{RT^2}dT + \sum_i \frac{\overline{G}_i^E}{RT}dn_i}$$

The fundamental excess-property relation

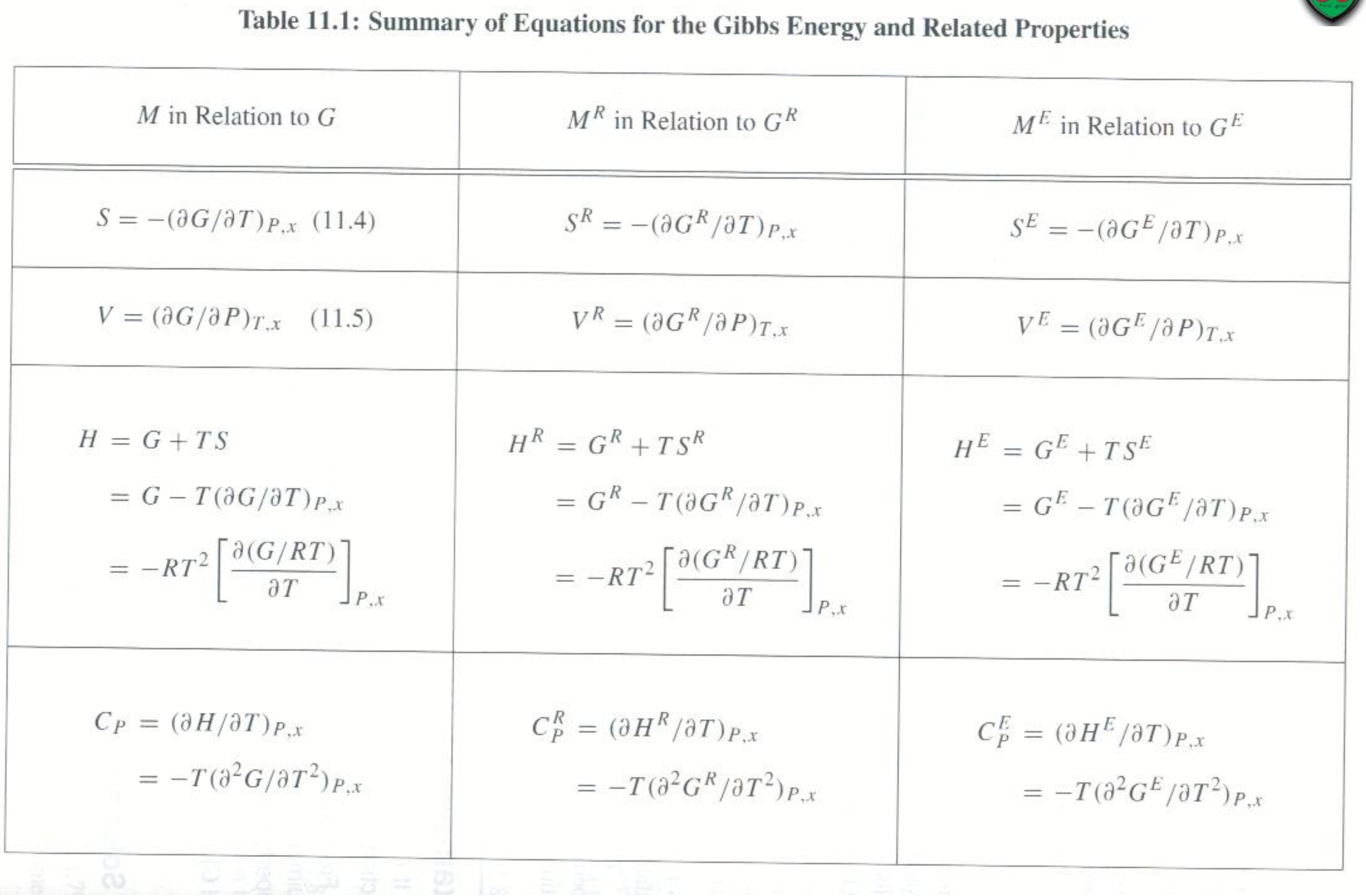


Table 11.1: Summary of Equations for the Gibbs Energy and Related Properties

M in Relation to G	M^R in Relation to G^R	M^E in Relation to G^E
$S = -(\partial G/\partial T)_{P,x}$ (11.4)	$S^R = -(\partial G^R/\partial T)_{P,x}$	$S^E = -(\partial G^E/\partial T)_{P,x}$
$V = (\partial G/\partial P)_{T,x}$ (11.5)	$V^R = (\partial G^R/\partial P)_{T,x}$	$V^E = (\partial G^E/\partial P)_{T,x}$
$H = G + TS$ $= G - T(\partial G/\partial T)_{P,x}$ $= -RT^2\left[\frac{\partial(G/RT)}{\partial T}\right]_{P,x}$	$H^R = G^R + TS^R$ $= G^R - T(\partial G^R/\partial T)_{P,x}$ $= -RT^2\left[\frac{\partial(G^R/RT)}{\partial T}\right]_{P,x}$	$H^E = G^E + TS^E$ $= G^E - T(\partial G^E/\partial T)_{P,x}$ $= -RT^2\left[\frac{\partial(G^E/RT)}{\partial T}\right]_{P,x}$
$C_P = (\partial H/\partial T)_{P,x}$ $= -T(\partial^2 G/\partial T^2)_{P,x}$	$C_P^R = (\partial H^R/\partial T)_{P,x}$ $= -T(\partial^2 G^R/\partial T^2)_{P,x}$	$C_P^E = (\partial H^E/\partial T)_{P,x}$ $= -T(\partial^2 G^E/\partial T^2)_{P,x}$

Example 11.10 (1) If C^E_P is a constant, independent of T, find expression for G^E, S^E, and H^E as functions of T. (2) From the equations developed in part (1), find values for G^E , S^E, and H^E for an equilmolar solution of benzene(1) / n-hexane(2) at 323.15K, given the following excess-property values for equilmolar solution at 298.15K: C^E_P =-2.86 J/mol-K, H^E = 897.9 J/mol, and G^E = 384.5 J/mol.

From Table 11.1:

$$\boxed{C_P^E = -T\left(\frac{\partial^2 G^E}{\partial T^2}\right)_{P,x}} \xrightarrow[\boxed{C_P^E = a = const.}]{} \boxed{\left(\frac{\partial^2 G^E}{\partial T^2}\right)_{P,x} = -\frac{a}{T}}$$

integration

$$\boxed{\left(\frac{\partial G^E}{\partial T}\right)_{P,x} = -a\ln T + b}$$

integration

$$\boxed{G^E = -a(T\ln T - T) + bT + c}$$

From Table 11.1:

$$\boxed{S^E = -\left(\frac{\partial G^E}{\partial T}\right)_{P,x}}$$

integration

$$\boxed{S^E = a\ln T - b}$$

$$\boxed{H^E = G^E + TS^E = aT + c}$$

At T=298.15 K:

$$\boxed{C_P^E = a = -2.86}$$

$$\boxed{897.9 = a(298.15) + c}$$

$$\boxed{384.5 = -a((298.15)\ln(298.15) - (298.15) + b(198.15) + c}$$

Solve to obtain:

a = -2.86

c= 1750.6

b= -18.0171

Example 11.10

$$\boxed{G^E = -a(T\ln T - T) + bT + c = 2.86(T\ln T - T) - 18.0171T + 1750.6}$$

$$\boxed{S^E = a\ln T - b = -2.86\ln T + 18.0171}$$

$$\boxed{H^E = aT + c = -2.86T + 1750.6}$$

At T=323.15 K:

G^E =344.4 J/mol

S^E =1.492 J/(mol.K)

H^E =826.4 J/mol

The excess Gibbs energy and the activity coefficient

- The excess Gibbs energy is of particular interest:

$$\boxed{G^E \equiv G - G^{id}}$$

$$\boxed{\bar{G}_i = \Gamma_i(T) + RT \ln \hat{f}_i}$$

$$\boxed{\bar{G}_i^{id} = \Gamma_i(T) + RT \ln x_i f_i}$$

$$\boxed{\bar{G}_i^E = RT \ln \frac{\hat{f}_i}{x_i f_i}}$$

$$\boxed{\gamma_i \equiv \frac{\hat{f}_i}{x_i f_i}}$$

The activity coefficient of species *i* in solution. A factor introduced into Raoult's law to account for liquid-phase non-idealities.

$$\boxed{\bar{G}_i^E = RT \ln \gamma_i}$$

For ideal solution, $\boxed{\bar{G}_i^E = 0, \quad \gamma_i = 1}$

Comparing to gas mixture: $\boxed{\bar{G}_i^R = RT \ln \hat{\phi}_i}$

The excess Gibbs energy and the activity coefficient

$$\boxed{d\left(\frac{nG^E}{RT}\right)=\frac{nV^E}{RT}dP-\frac{nH^E}{RT^2}dT+\sum_i\frac{\overline{G}_i^E}{RT}dn_i}\rightarrow\boxed{d\left(\frac{nG^E}{RT}\right)=\frac{nV^E}{RT}dP-\frac{nH^E}{RT^2}dT+\sum_i\ln\gamma_i dn_i}$$

$$\boxed{\frac{V^E}{RT}=\left(\frac{\partial(G^E/RT)}{\partial P}\right)_{T,x}}$$

$$\boxed{\frac{H^E}{RT}=-T\left(\frac{\partial(G^E/RT)}{\partial T}\right)_{P,x}}$$

$$\boxed{\ln\gamma_i=\left(\frac{\partial(nG^E/RT)}{\partial n_i}\right)_{P,T,n_j}}$$

Experimental accessible values:
activity coefficients from VLE data,
V^E and H^E values come from mixing experiments.

$\ln(\gamma_i)$ is a partial property of G^E/RT

The Gibbs/Duhem equation

$$\boxed{\overline{G}_i^E=RT\ln\gamma_i}\qquad\boxed{M=\sum_i x_i\overline{M}_i}\qquad\boxed{\left(\frac{\partial M}{\partial P}\right)_{T,n}dP+\left(\frac{\partial M}{\partial T}\right)_{P,n}dT-\sum_i x_i d\overline{M}_i=0}$$

$$\downarrow\qquad\qquad\downarrow$$

$$\underbrace{\boxed{\frac{G^E}{RT}=\sum_i x_i\ln\gamma_i}\qquad\boxed{\sum_i x_i d\ln\gamma_i=0\quad(const.\,T,\,P)}}_{\text{Important application in phase-equilibrium thermodynamics.}}$$

The nature of excess properties

How to obtain solution excess properties?

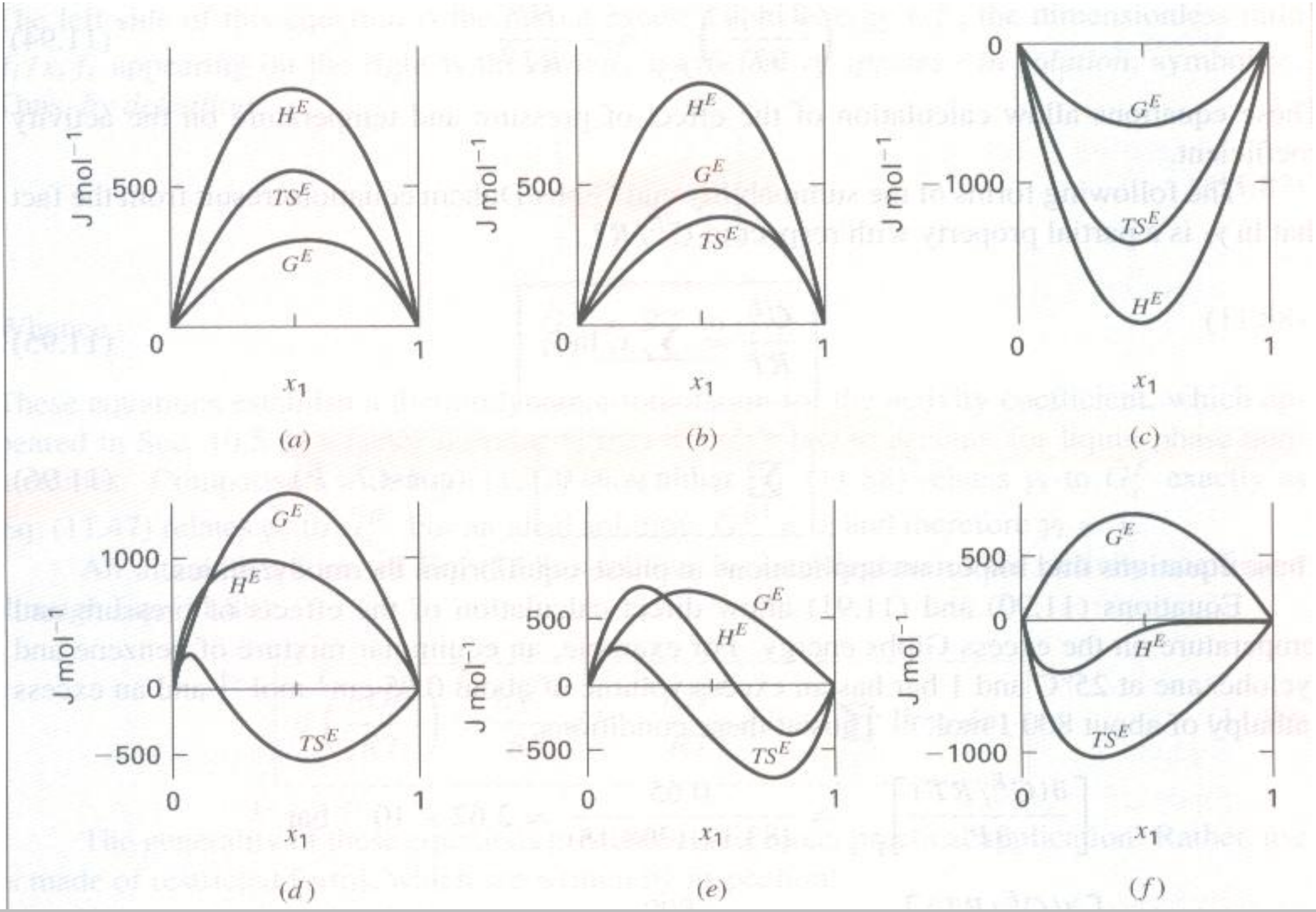
- G^E : through the data reduction of VLE experiments
- V^E : from mixing experiment
- H^E : from mixing experiment
- $S^E = (H^E - G^E) / T$

(Chapter 12)

▪ **Remember that excess properties are strong function of temperature.**

The nature of excess properties

Fig 11.4: Excess properties at 50 oC for six binary liquid systems:



The nature of excess properties

- **Important remarks on Fig 11.4:**
  - Excess properties become zero as either species approach purity.
  - G^E is approximately parabolic in shape; H^E and TS^E exhibit individualistic composition dependence.
  - When an excess property M^E has single sign (+ve or –ve), the extreme value of M^E often occurs near the equilmolar composition.