Termodinamika Larutan: Teori

(Solution Thermodynamics: Theory)

Lecturer: Bregas S T Sembodo

Pendahuluan

- Sistem nyata biasanya berupa campuran fluida
- Komposisi sering menjadi peubah (variabel) utama
- Dikembangkan teori dasar aplikasi termodinamika untuk campuran gas dan larutan
- Akan diperkenalkan:
  - Potensial kimia (chemical potential)
  - Sifat parsial (partial properties)
  - Fugasitas (fugacity)
  - Sifat ekses (excess properties)
  - Larutan ideal (ideal solution)

Hubungan sifat-sifat fundamental

- Hubungan antara Energi Gibbs dengan suhu dan tekanan pada sistem tertutup:

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

  - Diterapkan untuk fluida fase tunggal dalam sistem tertutup dimana tidak terjadi reaksi kimia.

- Untuk fase tunggal, sistem terbuka (a single-phase, open system):

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

Definisi potensial kimia: $\boxed{\mu_i \equiv \left[\dfrac{\partial(nG)}{\partial n_i}\right]_{P,T,n_j}}$

Hubungan sifat fundamental untuk sistem fluida fase tunggal dengan komposisi konstan maupun sebagai variabel:

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

Jika n = 1, $\boxed{dG = VdP - SdT + \sum_i \mu_i dx_i} \longrightarrow \boxed{G = G(P, T, x_1, x_2, \ldots, x_i, \ldots)}$

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

Energi Gibbs dinyatakan sbg fungsi dari variabel-variabel kanonis

Sifat larutan, M

Sifat parsial, $\bar{M}_i$

Sifat spesies murni, M_i

Potensial kimia dan kesetimbangan fase

- Untuk sistem tertutup terdiri dari 2 fase dalam kesetimbangan:

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

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

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

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

Neraca massa:

$$\boxed{dn_i^{\alpha} = -dn_i^{\beta}}$$

$$\boxed{\mu_i^{\alpha} = \mu_i^{\beta}}$$

Multi fase pada T dan P yg sama adalah dalam **kesetimbangan** jika **potensial kimia** setiap spesies pada semua fase **sama**.

Sifat Parsial (*Partial properties)*

- Definisi **sifat molar parsial** (*partial molar property*) spesies i :

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

arti : perubahan besaran M terhadap perubahan n_i (jml mol i) jika P, T dan n_j (jml mol spesies lain) tetap

  - Potensial kimia adalah Energi Gibbs molar parsial: $\boxed{\mu_i \equiv \overline{G}_i}$
  - Untuk sifat termodinamika M:

$$\boxed{nM = M(P,T,n_1,n_2,\ldots,n_i,\ldots)}$$

$$\downarrow$$

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

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

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

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

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

dan

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

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

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

Persamaan Gibbs/Duhem

$$nM - \sum_i n_i \overline{M}_i = 0$$

Perhitungan sifat-sifat campuran dari sifat-sifat parsialnya

Sifat Parsial pada Larutan Biner

- Untuk sistem biner

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

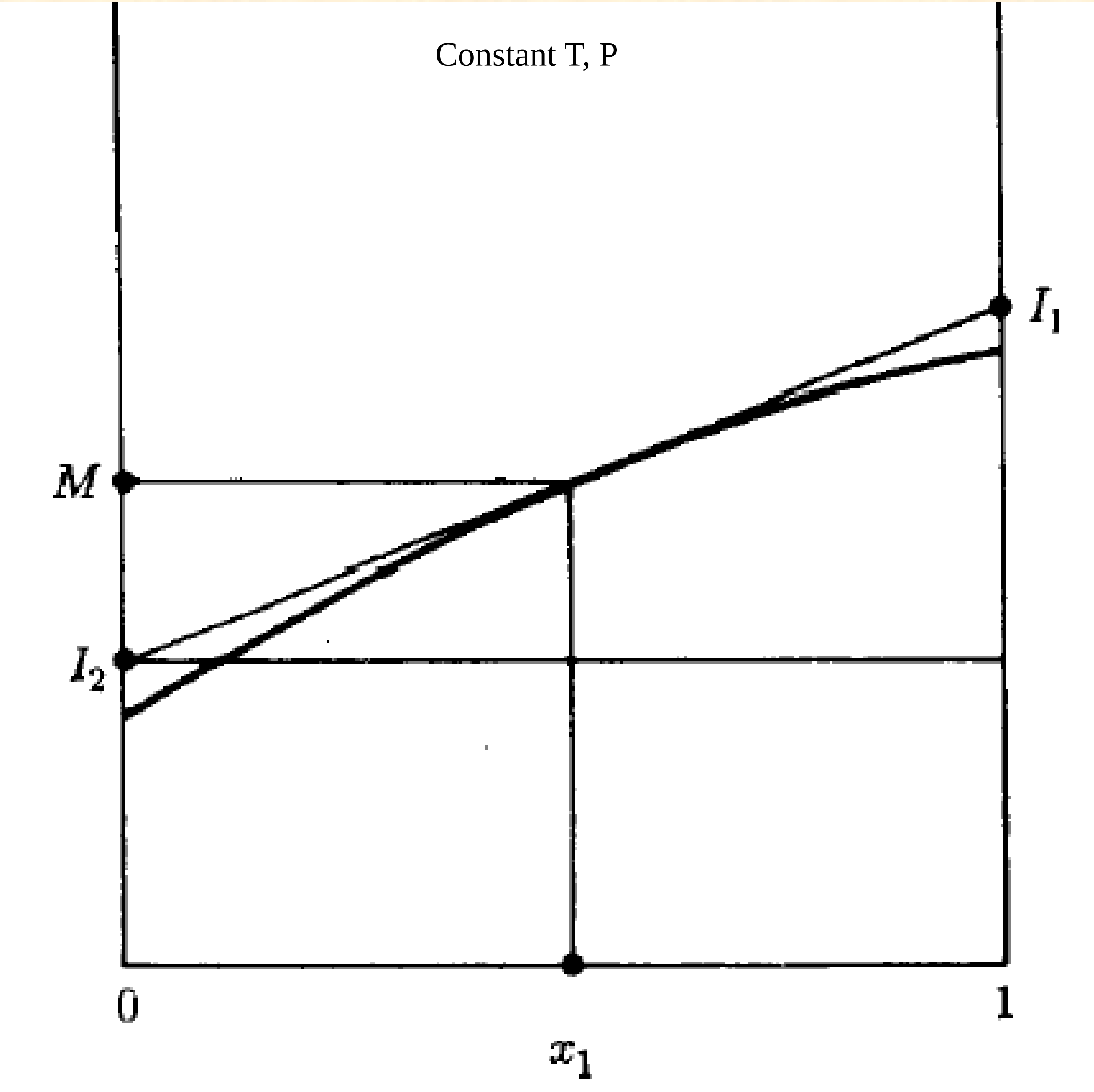
$$\boxed{dM = \cancel{x_1 d\bar{M}_1} + \bar{M}_1 dx_1 + \cancel{x_2 d\bar{M}_2} + \bar{M}_2 dx_2}$$

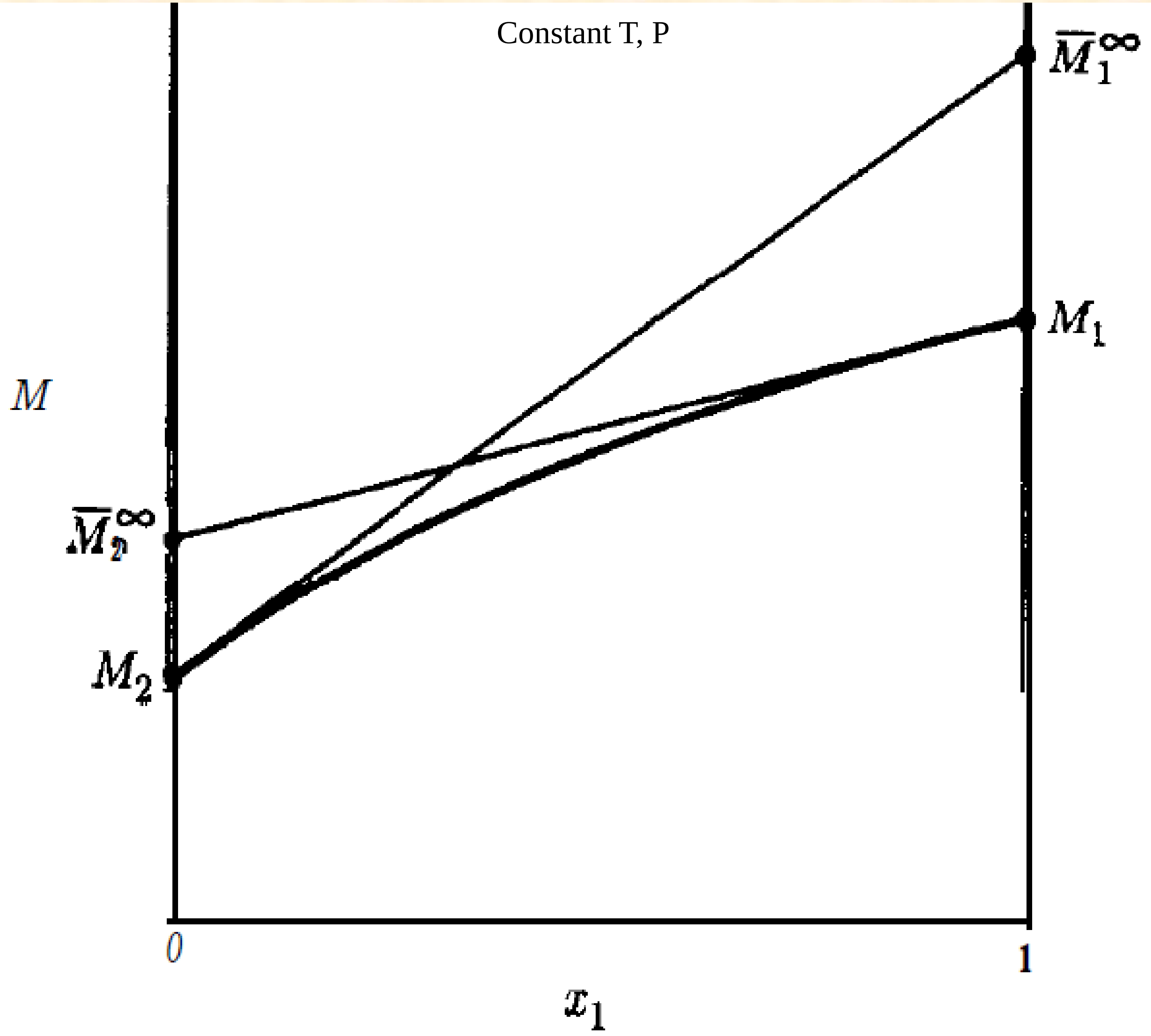
P and T tetap, menggunakan pers. Gibbs/Duhem

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

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

$$\boxed{\frac{dM}{dx_1} = \bar{M}_1 - \bar{M}_2} \longrightarrow \boxed{\bar{M}_1 = M + x_2\frac{dM}{dx_1}} \quad \boxed{\bar{M}_2 = M - x_1\frac{dM}{dx_1}}$$


Constant T, P

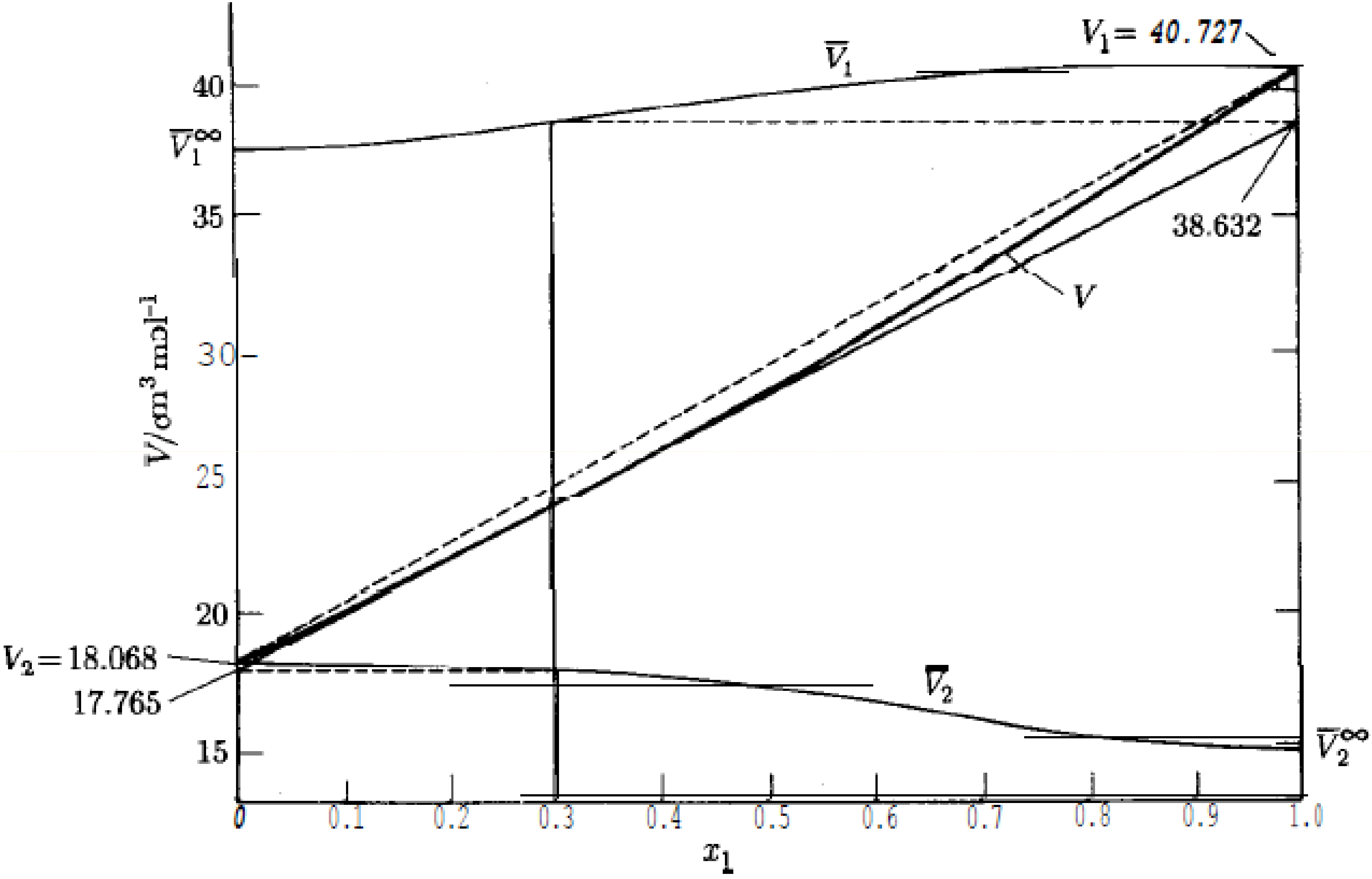

Constant T, P
$\overline{M}_1^\infty$
M_1
M
$\overline{M}_2^\infty$
M_2
0
1
x_1

Pada suatu Lab dibutuhkan 2000 cm^3 antifreeze solution (larutan antibeku) mengandung 30 mol-% metanol dalam air. Berapa volume metanol murni dan air murni pada 25°C harus dicampur untuk memperoleh 2000 cm^3 antifreeze pada 25°C? Volume molar parsial dan volume murni masing-masing spesies diketahui.

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

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

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

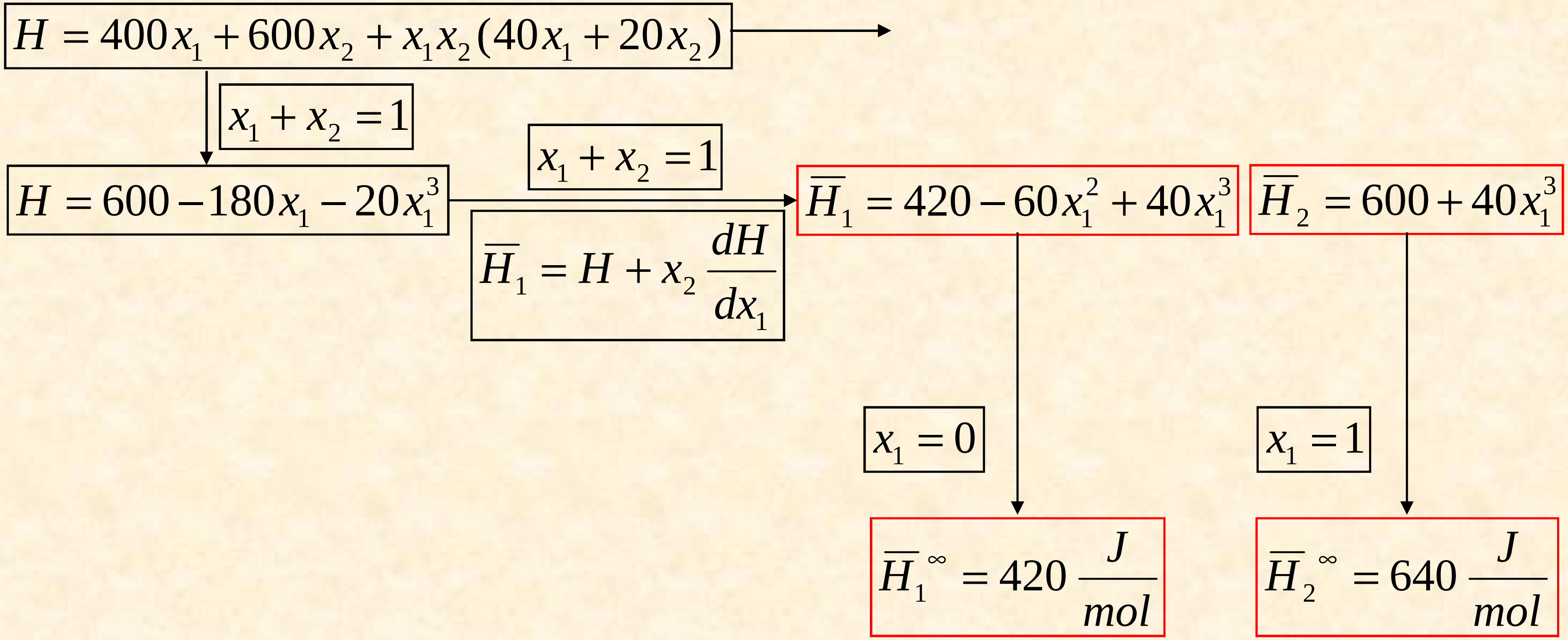


$V_1 = 40.727$
$\overline{V}_1$
40
$\overline{V}_1^{\infty}$
35
38.632
V
30
$V/\mathrm{cm^3\,mol^{-1}}$
25
20
$V_2 = 18.068$
17.765
$\overline{V}_2$
15
$\overline{V}_2^{\infty}$
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
x_1

Entalpi sistem cairan biner dari spesies 1 dan 2 pada T dan P tertentu adalah:

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

Tentukan $\overline{H}_1$ dan $\overline{H}_2$ sbg fungsi x_1, nilai numerik entalpi spesies murni H_1 and H_2, nilai numerik entalpi parsial pada pengenceran tak berhingga $\overline{H}_1^{\infty}$ dan $\overline{H}_2^{\infty}$



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

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

$$\boxed{H = 600 - 180x_1 - 20x_1^3}$$

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

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

$$\boxed{\overline{H}_1 = 420 - 60x_1^2 + 40x_1^3} \qquad \boxed{\overline{H}_2 = 600 + 40x_1^3}$$

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

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

Hubungan antar Sifat Parsial

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

- Relasi Maxwell :

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

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

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

$$\longrightarrow \boxed{d\overline{G}_i = \overline{V}_i dP - \overline{S}_i dT}$$

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

Campuran Gas Ideal

- Teorema Gibbs’s
  - Sifat molar parsial spesies (kecuali volume) dalam camp. gas ideal SAMA DENGAN sifat molarnya sbg gas ideal murni pada suhu campuran tetapi pada tekanan yg sama dengan tekanan parsialnya dalam campuran.

$$\boxed{\overline{M}_i^{ig} \neq \overline{V}_i^{ig}}$$

$$\boxed{\overline{M}_i^{ig}(T,P) = M_i^{ig}(T,p_i)}$$

Untuk yg tidak tergantung tekanan, mis.

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

Untuk yg tergantung tekanan, mis. $\boxed{dS_i^{ig}=-Rd\ln P \quad const.T}$

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

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

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

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

$$\downarrow$$

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

or

$$\boxed{G^{ig}=\sum_i y_i\Gamma_i(T)+RT\sum_i y_i\ln y_iP} \longleftarrow \boxed{\mu_i^{ig}=\Gamma_i(T)+RT\ln y_iP} \boxed{G_i^{ig}=\Gamma_i(T)+RT\ln P}$$

$$S^{ig} = \sum_i y_i S_i^{ig} - R \sum_i y_i \ln y_i$$

$$S^{ig} - \sum_i y_i S_i^{ig} = -R \sum_i y_i \ln y_i = R \sum_i y_i \ln \frac{1}{y_i} = \Delta S \quad > 0$$

Perubahan entropi pencampuran gas ideal selalu positif ATAU entropi campuran gas ideal lebih besar dari pada entropi spesies murni konstituennya

Fugasitas dan Koefisien Fugasitas

- Potensial kimia: $$\boxed{\mu_i \equiv \left[\frac{\partial(nG)}{\partial n_i}\right]_{P,T,n_j}}$$
  - Menyediakan kriteria dasar kesetimbangan fase
  - Namun, Energi Gibbs juga μ_i didefinisikan berhubungan dengan energi dalam dan entropi (nilai absolut tidak diketahui, sulit ditentukan nilainya dari T dan P).
- Fugasitas: $$\boxed{G_i \equiv \Gamma_i(T) + RT \ln f_i}$$
  - Suatu kunatitas yg menggantikan μ_i

Dengan satuan tekanan

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

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

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

Residual Gibbs energy

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

Fugacity coefficient

$$\Big\downarrow$$

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

Kesetimbangan Uap-Cair (VLE) untuk Spesies Murni

- Uap Jenuh: $$\boxed{G_i^v = \Gamma_i(T) + RT \ln f_i^v}$$
- Cairan Jenuh: $$\boxed{G_i^l = \Gamma_i(T) + RT \ln f_i^l}$$

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

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

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

$$\Big\downarrow$$

$$\boxed{f_i^v = f_i^l = f_i^{sat}}$$

$$\boxed{\phi_i^v = \phi_i^l = \phi_i^{sat}}$$

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

Fugasitas Cairan Murni

- Fugasitas spesies murni *i* sebagai cairan tertekan (compressed liquid):

$$\boxed{G_i - G_i^{sat} = RT \ln \frac{f_i}{f_i^{sat}}} \qquad \boxed{G_i - G_i^{sat} = \int_{P_i^{sat}}^{P} V_i dP \quad (isothermal \;\; process)}$$

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

Karena V_i sedikit dipengaruhi P (weak function)

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

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

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

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 reference state:

$$\boxed{G_i^* = \Gamma_i(T) + RT \ln f_i^*}$$

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

The low pressure (say 1 kPa) at 300°C: $\boxed{f_i^* = P^* = 1\,kPa}$ $\boxed{S_i^* = 10.3450\ {}^{J}\!/_{gK}}$

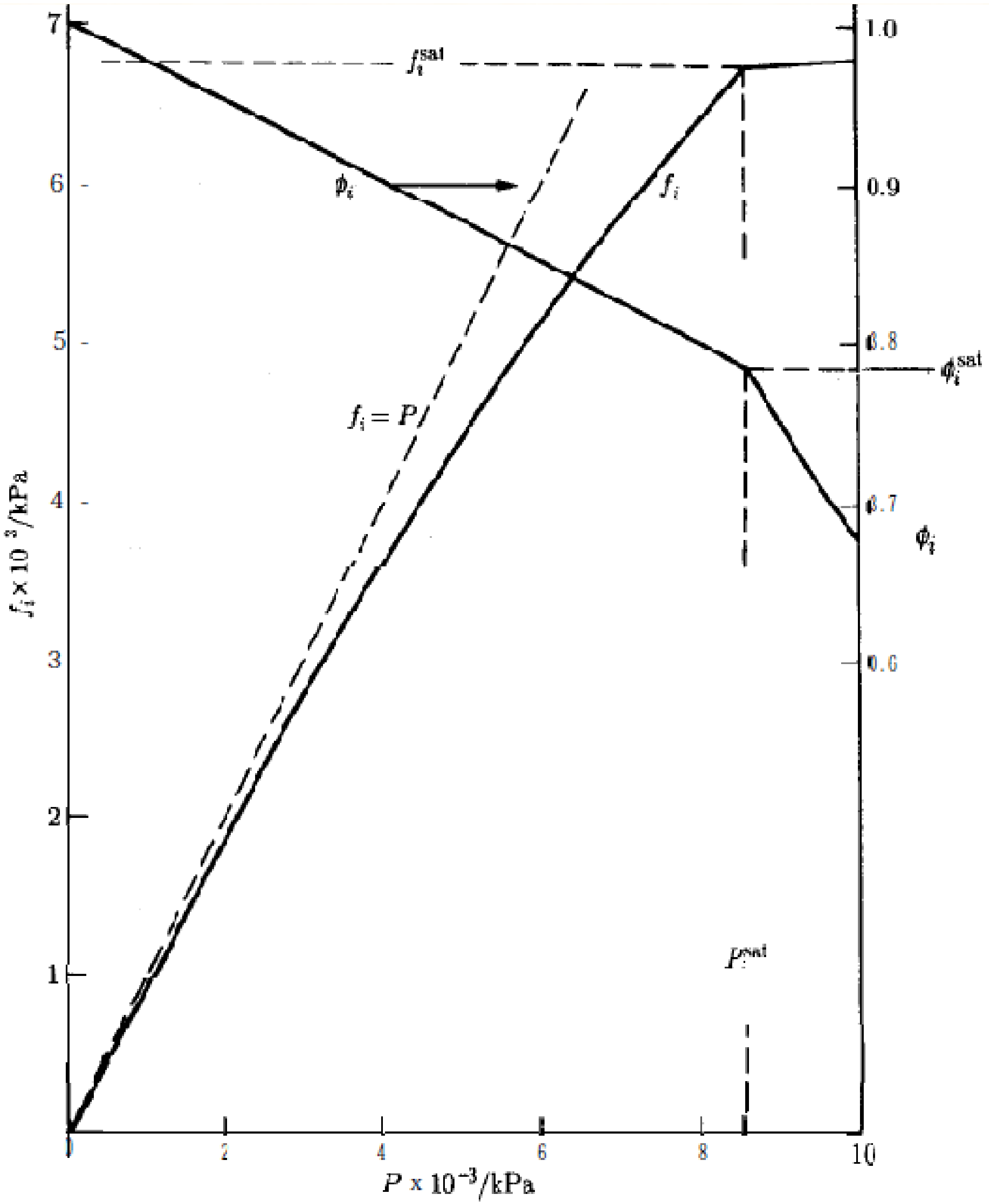
$$\boxed{H_i^* = 3076.8\ {}^{J}\!/_{g}}$$

For different values of P up to the saturated pressure at 300°C, one obtains the values of f_i ,and hence φ_i . Note, values of f_i and φ_i at 8592.7 kPa are obtained

Values of f_i and φ_i at higher pressure:

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

Fig 11.3


f_i^{sat}
ϕ_i
f_i
$f_i = P$
ϕ_i^{sat}
ϕ_i
P_i^{sat}
$f_i \times 10^{-3}$/kPa
$P \times 10^{-3}$/kPa
7
6
5
4
3
2
1
0
2
4
6
8
10
1.0
0.9
0.8
0.7
0.6

Fugasitas dan Koefisien Fugasitas: spesies dalam larutan

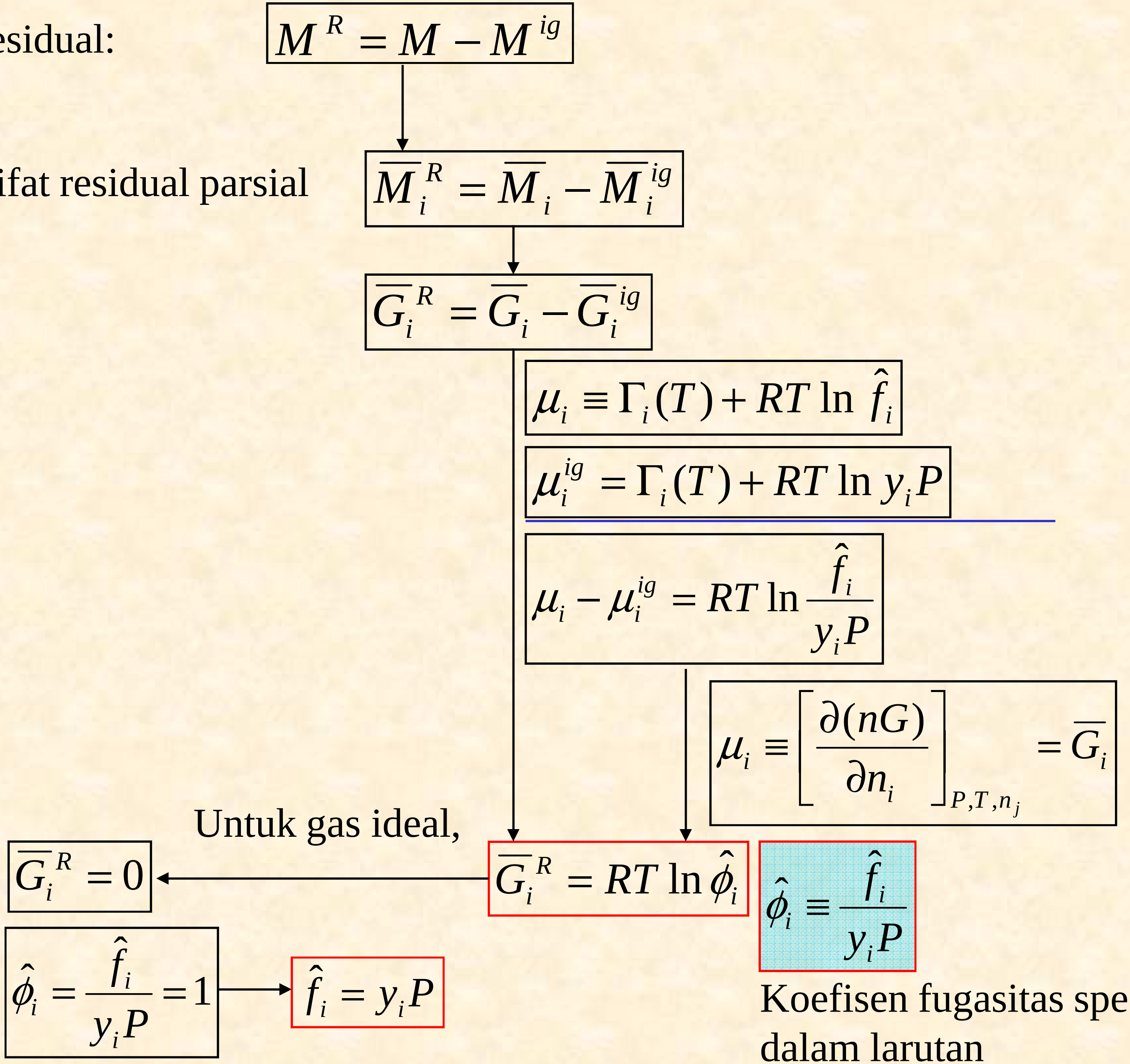
- Untuk spesies *i* dalam campuran gas nyata atau dalam larutan cair:

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

Fugasitas spesies *i* dalam larutan
(mengganti tekanan parsial y_iP)

- Multi fase pada T dan P yg sama adalah dalam **kesetimbangan** jika fugasitas masing-masing spesies konstituen **sama** pada semua fase:

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



Sifat Residual:

$$M^R = M - M^{ig}$$

Sifat residual parsial

$$\bar{M}_i^R = \bar{M}_i - \bar{M}_i^{ig}$$

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

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

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

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

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

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

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

Koefisen fugasitas spesies i dalam larutan

Untuk gas ideal,

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

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

$$\hat{f}_i = y_i P$$

Fundamental residual-property relation

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

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

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

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

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:

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

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

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

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 E.O.S

- 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: $\boxed{B = y_1 y_1 B_{11} + y_1 y_2 B_{12} + y_2 y_1 B_{21} + y_2 y_2 B_{22}}$
- *n* mol of gas mixture: $\boxed{nZ = n + \frac{nBP}{RT}}$

$$\downarrow$$

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

$$\downarrow$$

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

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

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

$$\boxed{\delta_{12} \equiv 2B_{12} - B_{11} - B_{22}} \quad \boxed{y_i = n_i / n}$$

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

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

For multicomponent gas mixture, the general form:

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

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

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.

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

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

$$\downarrow$$

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

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

$$\downarrow$$

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

Generalized correlations for the fugacity coefficient

$$\boxed{\ln \phi_i = \int_0^{P_r} (Z_i - 1)\frac{dP_r}{P_r} \quad (const.\, T_r)} \xrightarrow{\boxed{Z - 1 = \frac{P_r}{T_r}(B^0 + \omega B^1)}} \boxed{\ln \phi = \frac{P_r}{T_r}(B^0 + \omega B^1)}$$

$$\Big\downarrow$$

$$\boxed{\phi = PHIB(TR, PR, OMEGA)}$$

For pure gas

$$\Big\downarrow \boxed{Z = Z^0 + \omega Z^1}$$

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

or

$$\boxed{\ln \phi = \ln \phi^0 + \omega \ln \phi^1}$$

with

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

For pure gas

Table E1:E4 or Table E13:E16

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

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

Table E15 and E16

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

For gas mixture:

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

$$\boxed{B_{ij} = \frac{RT_{cij}}{P_{cij}}(B^0 + \omega_{ij} B^1)} \quad \boxed{\omega_{ij} = \frac{\omega_i + \omega_j}{2}}$$

Empirical interaction parameter

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

Prausnitz et al. 1986

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

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 $k_{ij} = 0$.

$$\boxed{\omega_{ij} = \frac{\omega_i + \omega_j}{2}} \quad \boxed{Z_{cij} = \frac{Z_{ci} + Z_{cj}}{2}} \quad \boxed{P_{cij} = \frac{Z_{cij} RT_{cij}}{V_{cij}}} \quad \boxed{V_{cij} = \left(\frac{V_{ci}^{1/3} + V_{cj}^{1/3}}{2}\right)^3}$$

$$\boxed{B_{ij} = \frac{RT_{cij}}{P_{cij}}(B^0 + \omega_{ij} B^1)} \quad \boxed{T_{cij} = \sqrt{(T_{ci} T_{cj})}(1 - k_{ij})} \quad \boxed{\delta_{12} \equiv 2B_{12} - B_{11} - B_{22}}$$

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

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

The ideal solution

- Serves as a standard to be compared:

$$\boxed{M^{id} = \sum_i x_i \overline{M}_i^{id}}$$

$$\boxed{\overline{G}_i^{id} = G_i + RT\ln x_i} \longrightarrow \boxed{G^{id} = \sum_i x_i G_i + RT\sum_i x_i \ln x_i}$$

cf. $\boxed{\overline{G}_i^{ig} = G_i^{ig} + RT\ln y_i}$

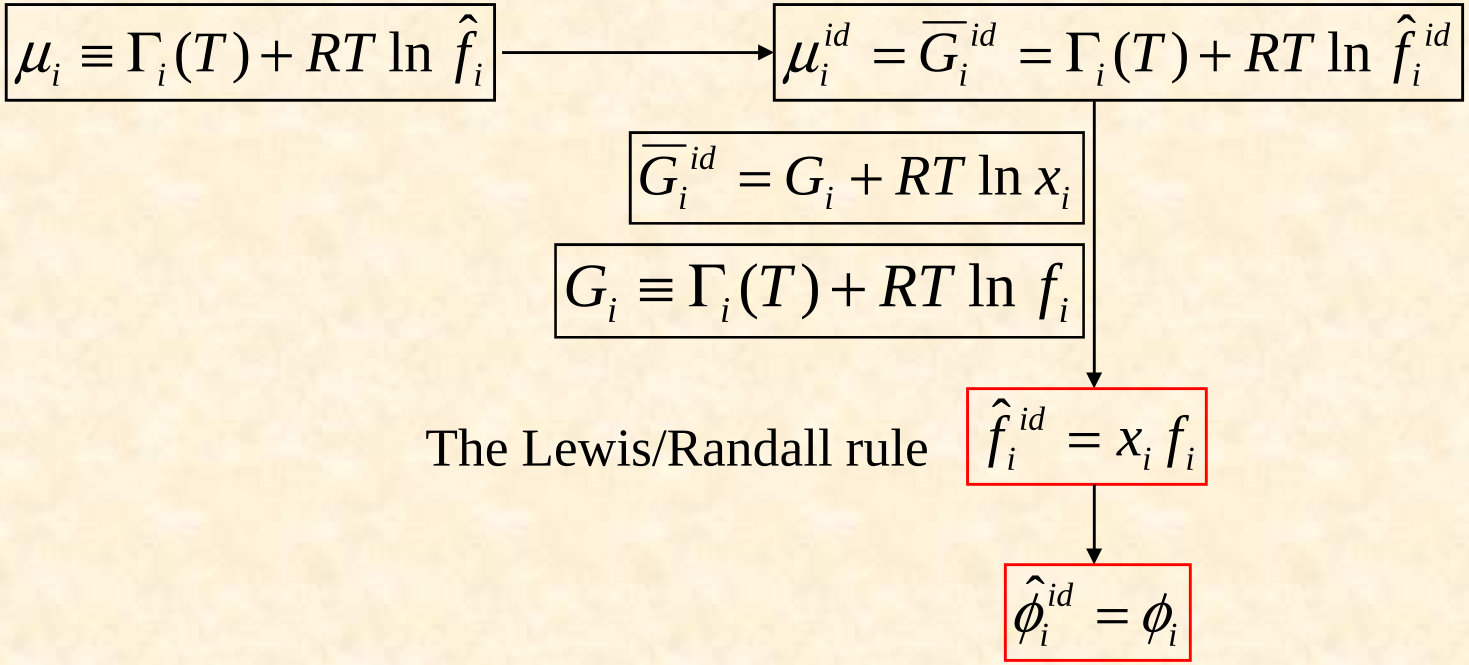
$$\boxed{\overline{S}_i^{id} = -\left(\frac{\partial \overline{G}_i^{id}}{\partial T}\right)_{P,x} = -\left(\frac{\partial G_i}{\partial T}\right)_P - R\ln x_i} \longrightarrow \boxed{\overline{S}_i^{id} = S_i - R\ln x_i} \boxed{S^{id} = \sum_i x_i S_i - R\sum_i x_i \ln x_i}$$

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

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

The Lewis/Randall Rule

- For a special case of species *i* in an ideal solution:



$$\boxed{\mu_i \equiv \Gamma_i(T) + RT \ln \hat{f}_i} \longrightarrow \boxed{\mu_i^{id} = \overline{G}_i^{id} = \Gamma_i(T) + RT \ln \hat{f}_i^{id}}$$

$$\boxed{\overline{G}_i^{id} = G_i + RT \ln x_i}$$

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

The Lewis/Randall rule $\boxed{\hat{f}_i^{id} = x_i f_i}$

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

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, we have:

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

The fundamental excess-property relation

(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), fine 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

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

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

$$\left.\begin{array}{l}
\boxed{C_P^E = a = -2.86} \\
\boxed{897.9 = a(298.15) + c} \\
\boxed{384.5 = -a((298.15)\ln(298.15) - (298.15) + b(198.15) + c}
\end{array}\right\}$$

We have values of a, b, c and hence the excess-properties at 323.15K

The excess Gibbs energy and the activity coefficient

- The excess Gibbs energy is of particular interest:

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

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

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

$$\Big\downarrow$$

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

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

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

$$\Big\downarrow$$

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

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

c.f. $\boxed{\overline{G}_i^{\,R} = RT \ln \hat{\phi}_i}$

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

$$\downarrow$$

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

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

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

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

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

$$\boxed{\frac{G^E}{RT}=\sum_i x_i\ln\gamma_i}$$

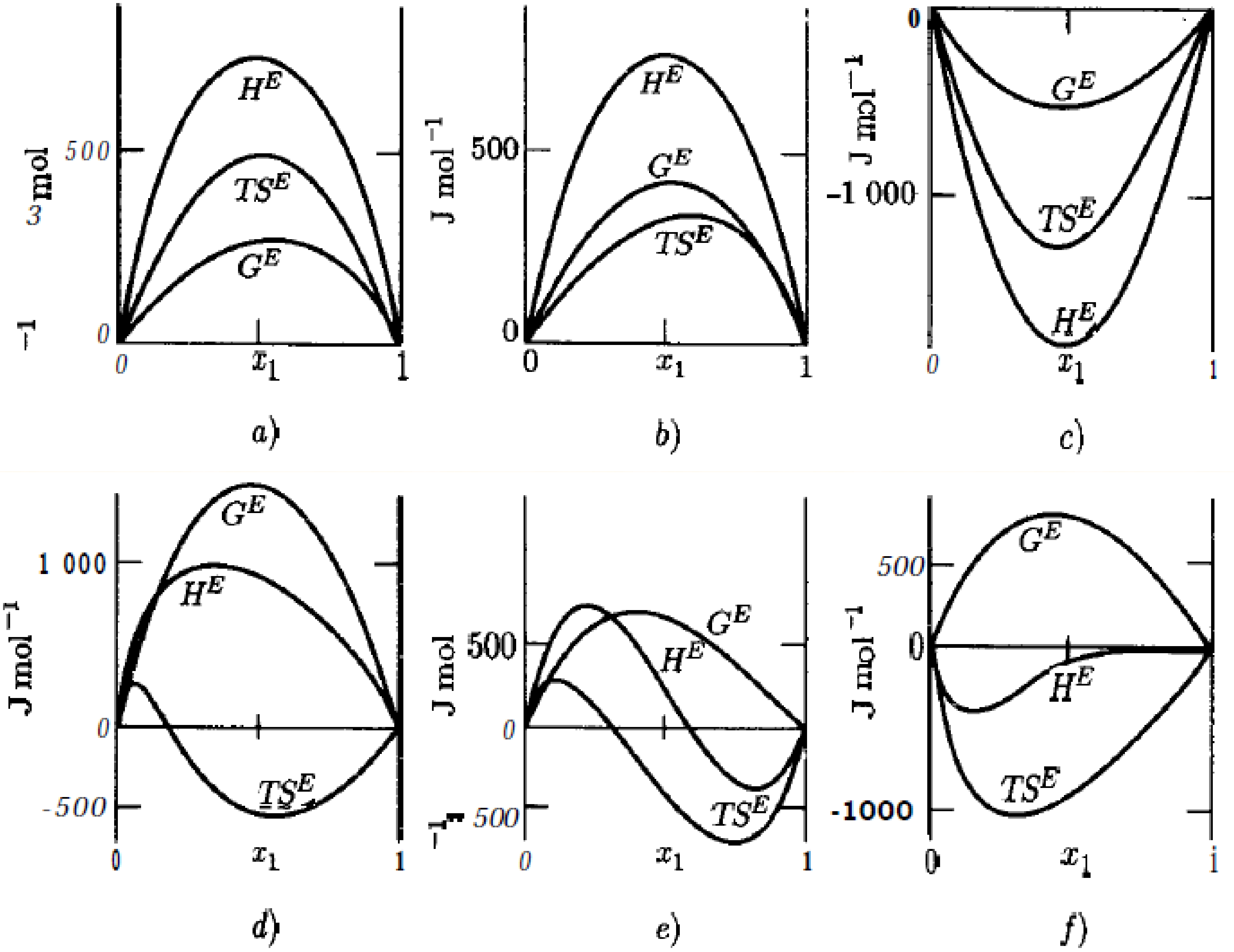
$$\boxed{\sum_i x_i d\ln\gamma_i=0\quad(const.\,T,\,P)}$$

Important application in phase-equilibrium thermodynamics.

The nature of excess properties

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

- Fig 11.4
  - excess properties become zero as either species ~ 1.
  - G^E is approximately parabolic in shape; H^E and TS^E exhibit individual composition dependence.
  - The extreme value of M^E often occurs near the equilmolar composition.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x_1
1
H^E
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a)
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