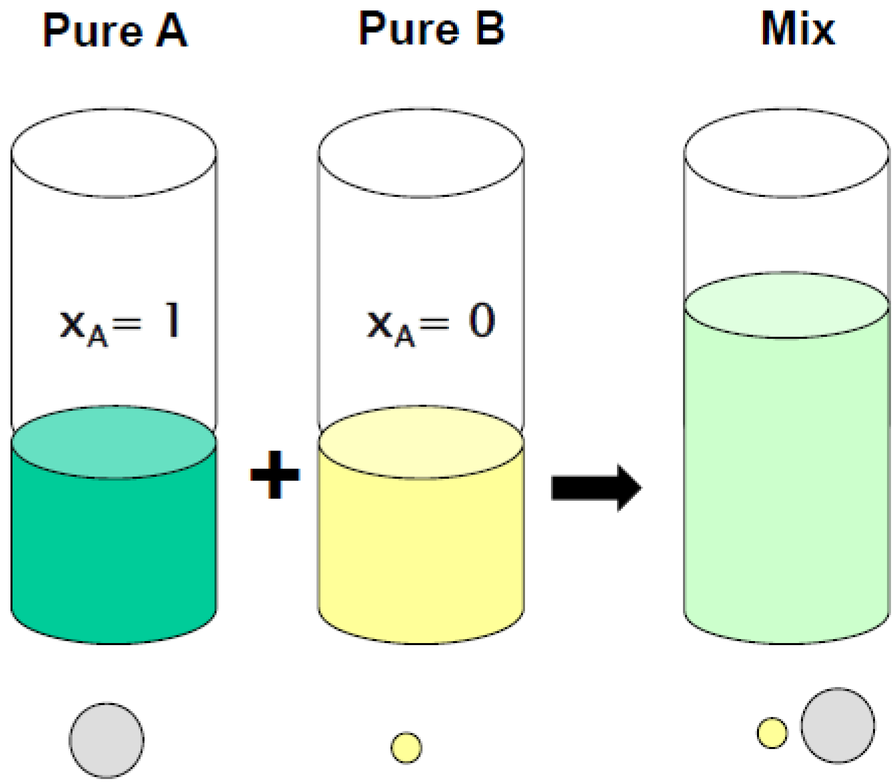
L12 Mixture properties

Mixtures

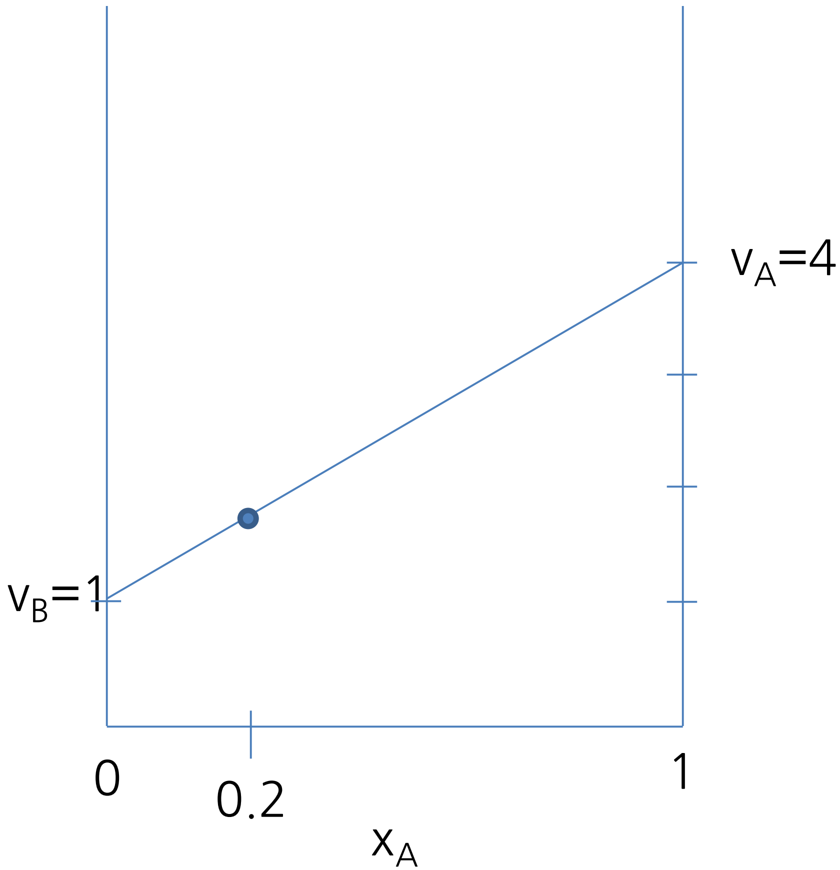


In Mixture,
x_A=0.2
x_B=0.8

n (mol)	100	400	500
V (m^3)	400	400	?
v(m^3/mol)	4	1	?/500

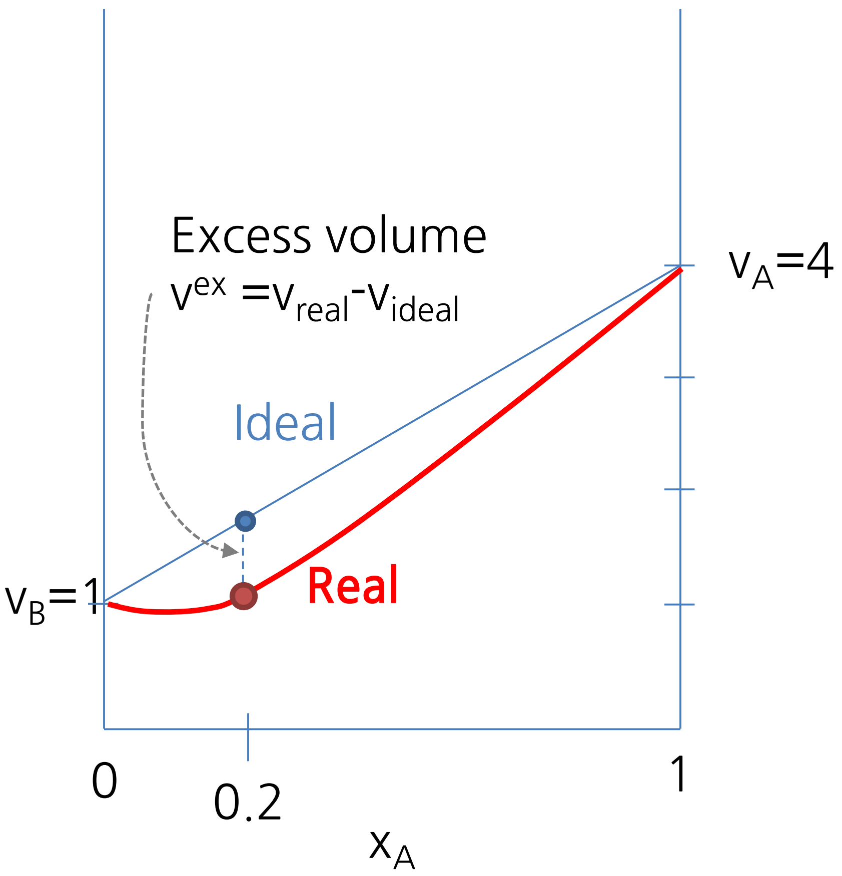
Volume of an ideal mixture

- $v_{ideal} = x_A v_A + x_B v_B = 1.6$

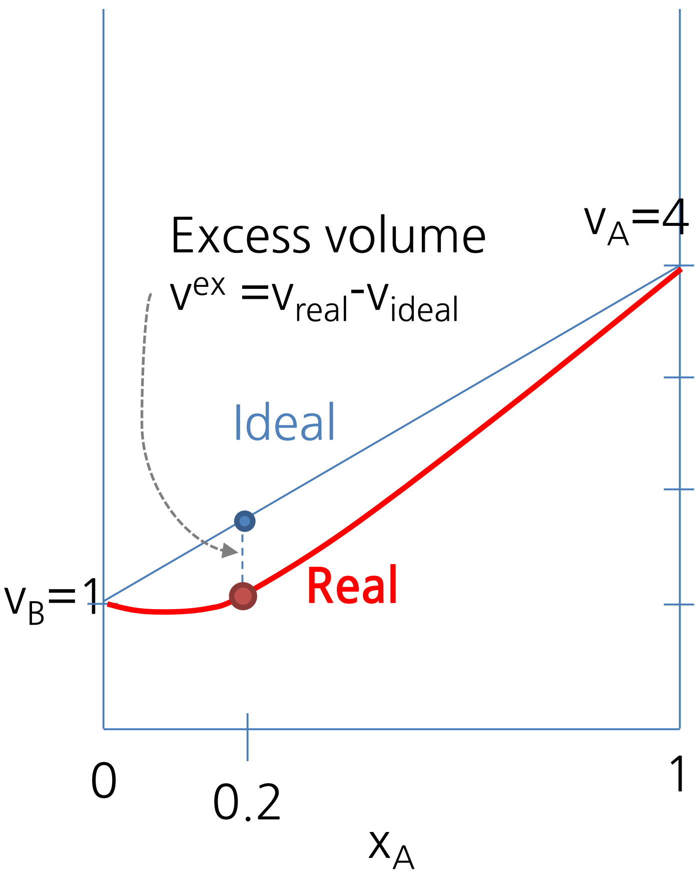


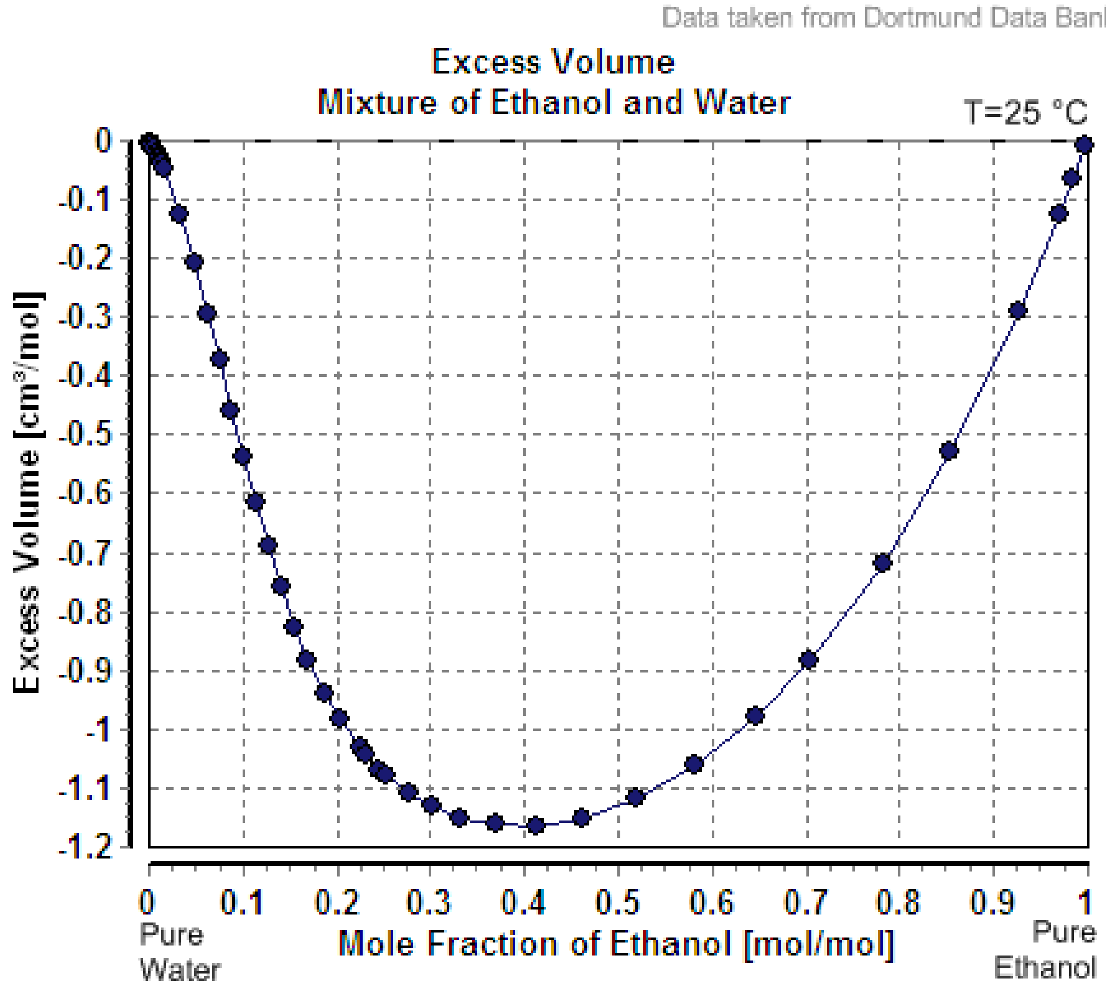
n (mol)	100	400	500
V (m^3)	400	400	800
v(m^3/mol)	4	1	1.6

Volume of a real mixture



Excess volume for ethanol/water

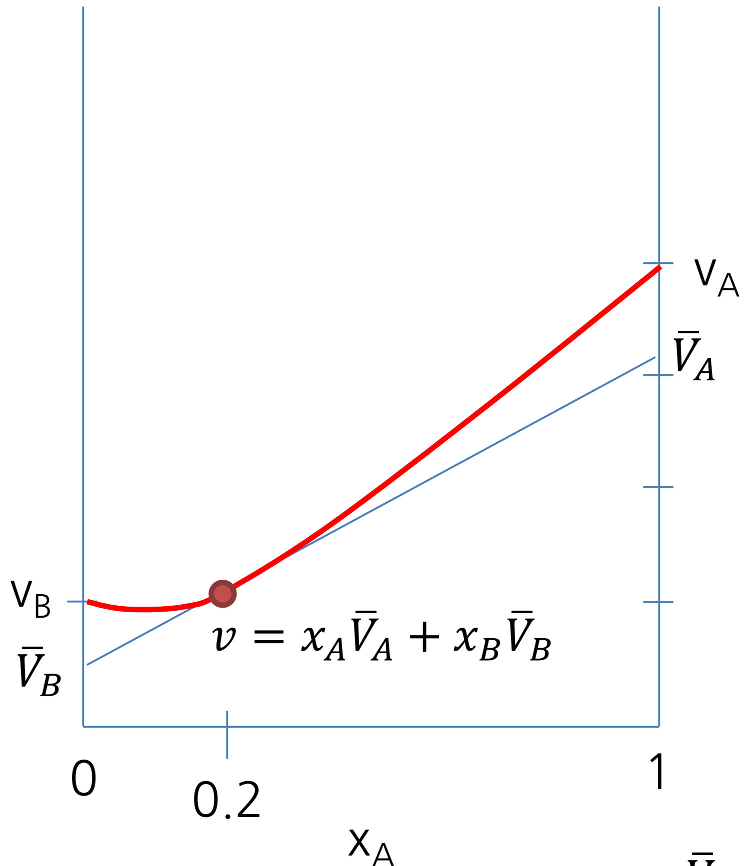




Partial Molar Volume $\bar{V}$

- $\bar{V}_A = \left(\frac{\partial V}{\partial n_A}\right)_{T,P,n_B}$
- The volume change of a mixture when one mole of A added to the mixture.
- T, P, number of other molecules are constant. (only number of A molecule is change)

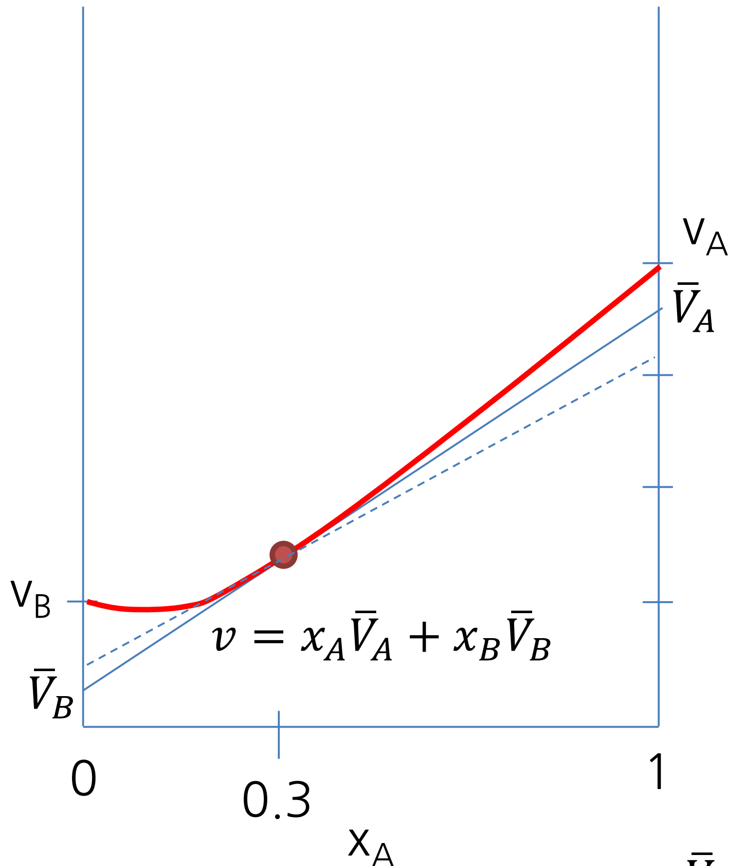
Partial Molar Volume



$$\bar{V}_B = v - x_A \frac{dv}{dx_A}$$

$$\bar{V}_A = v + (1 - x_A) \frac{dv}{dx_A}$$

Partial Molar Volume varies with composition

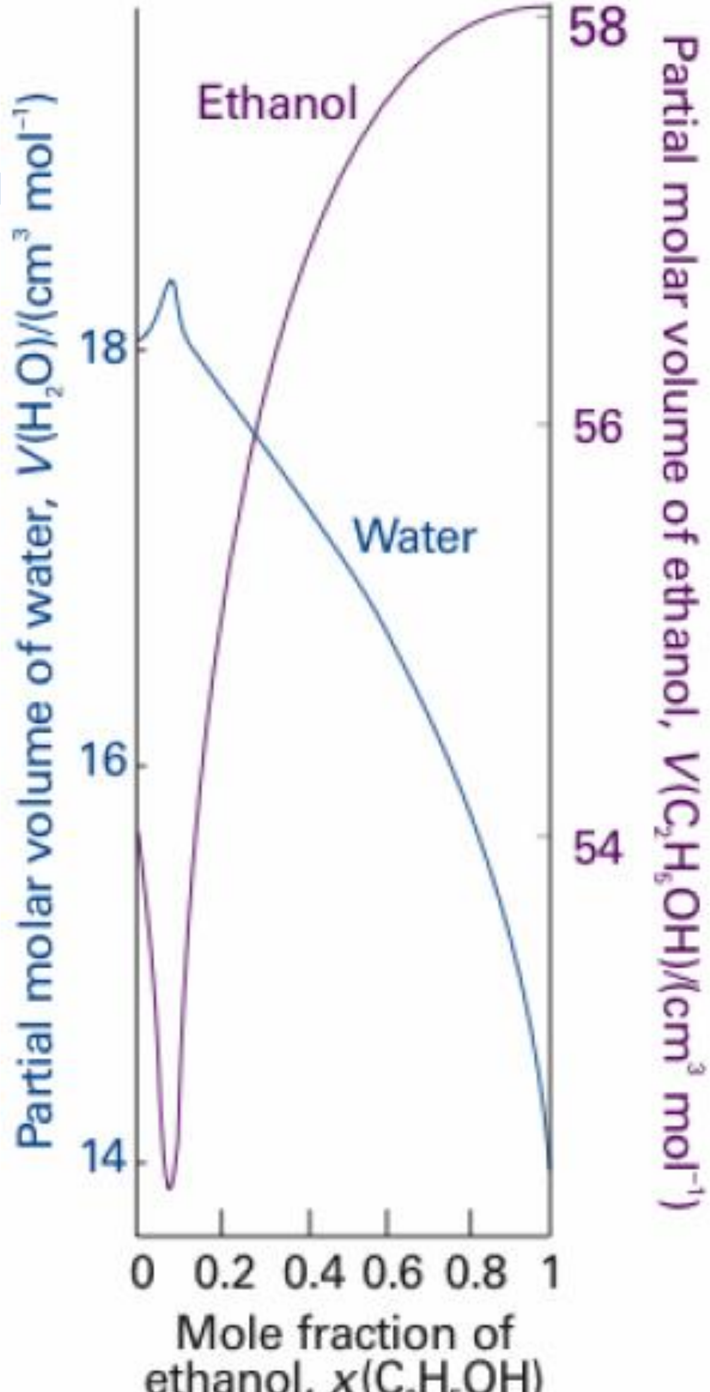


$$\bar{V}_B = v - x_A\frac{dv}{dx_A}$$

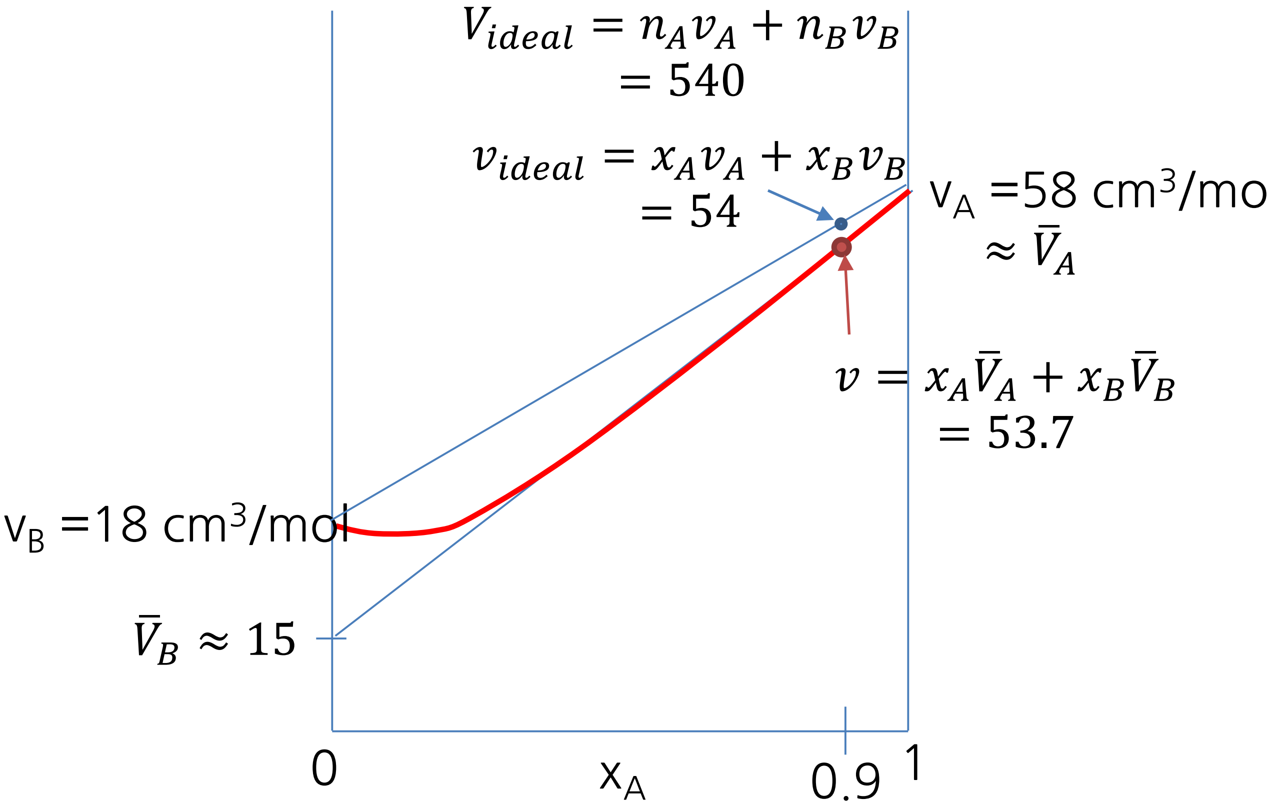
$$\bar{V}_A = v + (1 - x_A)\frac{dv}{dx_A}$$

Water/Ethanol Mixture

- 1 mole of water mixed with 9 moles of ethanol
- mole fraction of ethanol=?
- partial molar volume
  - for ethanol≈?
  - for water≈?
- Molar volume of mixture =?
- an excess volume=?



Water/Ethanol Mixture



Partial Molar Volume

- For a pure substance,
  - $v = f(T, P)$
  - $dv = \left(\frac{\partial v}{\partial T}\right)_P dT + \left(\frac{\partial v}{\partial P}\right)_T dP$
- For a mixture with m species,
  - $V = f(T, P, n_1, n_2, n_3, \ldots, n_m)$

$$dV = \left(\frac{\partial V}{\partial T}\right)_{P,n} dT + \left(\frac{\partial V}{\partial P}\right)_{T,n} dP + \left(\frac{\partial V}{\partial n_1}\right)_{T,P,n_2,n_3 \ldots n_m} dn_1 + \left(\frac{\partial V}{\partial n_2}\right)_{T,P,n_1,n_3 \ldots n_m} dn_2 + \cdots + \left(\frac{\partial V}{\partial n_m}\right)_{T,P,n_1,\ldots n_{m-1}} dn_m$$

$$= \left(\frac{\partial V}{\partial T}\right)_{P,n} dT + \left(\frac{\partial V}{\partial P}\right)_{T,n} dP + \sum_{i=1}^{m} \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j\neq i}} dn_i$$

Partial Molar Volume

- $dV = \left(\frac{\partial V}{\partial T}\right)_{P,n} dT + \left(\frac{\partial V}{\partial P}\right)_{T,n} dP + \sum_{i=1}^{m} \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j \neq i}} dn_i$
- If we define partial molar volume

$$\bar{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j \neq i}}$$

- $dV = \left(\frac{\partial V}{\partial T}\right)_{P,n} dT + \left(\frac{\partial V}{\partial P}\right)_{T,n} dP + \sum_{i=1}^{m} \bar{V}_i \, dn_i$

Thermodynamic properties of mixture

- At constant T, P,
  - $V = \sum \bar{V}_i n_i , \bar{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j\neq i}}$
  - $U = \sum \bar{U}_i n_i , \bar{U}_i = \left(\frac{\partial U}{\partial n_i}\right)_{T,P,n_{j\neq i}}$
  - $H = \sum \bar{H}_i n_i , \bar{H}_i = \left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_{j\neq i}}$
  - $S = \sum \bar{S}_i n_i , \bar{S}_i = \left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_{j\neq i}}$
  - $G = \sum \bar{G}_i n_i , \bar{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}}$

Ex 6.8

- HYSYS

	Δh_{mix}
NRTL	0

Ex 6.11

1atm, 25C	Δs_mix (HYSYS)	Δs_mix= $-R\sum y_i \ln y_i$
C1:C2 (5:5), PR	5.76	5.762
C1:C4 (5:5), PR	5.73	5.762
Ar:Ne (5:5), PR	5.76	5.762