

Excess Thermodynamic function.

Excess-thermodynamic functions can be defined as the thermodynamic functions of real solution minus the respective functions of ideal solutions. Excess-thermodynamic are indicators of the extent to which the real solution deviate from ideality, ideal solution.

Let us consider any function Y . If $\Delta Y_{mix}^{(real)}$ is the thermodynamic function of mixing for real system. and $\Delta Y_{mix}^{(ideal)}$ is the function of mixing of ideal system.

Then Y^E (Excess function) is -

Tuesday

$$Y^E = \Delta Y_{mix}^{(Real)} - \Delta Y_{mix}^{(Ideal)}$$

at same temperature and pressure

Different excess functions,

Excess

i) Chemical Potential

$$\mu_i^E = \mu_{real} - \mu_{ideal}$$

we know

$$\mu_{ideal} = \mu^0 + RT \ln x_i$$

~~$$\mu_i^E = \mu_i + RT$$~~

$$\mu_{Real} = \mu^0 + RT \ln a_i$$

$$\mu_i^E = (\mu_i^0 + RT \ln a_i) - (\mu_i^0 + RT \ln x_i)$$

11
Wednesday

September '02

$$\begin{aligned} &= (\mu_i^\circ + RT \ln \gamma_i x_i) - (\mu_i^\circ + RT \ln x_i) \quad \text{we have} \\ &= (\mu_i^\circ + RT \ln \gamma_i + RT \ln x_i) - (\mu_i^\circ + RT \ln x_i) \end{aligned}$$

$$\mu_i^E = \cancel{\mu_i^\circ} + RT \ln \gamma_i + RT \ln x_i - \cancel{\mu_i^\circ} - RT \ln x_i$$

$$\boxed{\mu_i^E = RT \ln \gamma_i}$$

11

Excess Gibbs free energy (G^E)

$$G^E = \Delta G_{\text{Real}}^{\text{mixing}} - \Delta G_{\text{ideal}}^{\text{mixing}}$$

$$= RT \sum n_i \ln a_i - RT \sum n_i \ln x_i$$

$$= RT \left[\sum n_i \ln a_i - \sum n_i \ln x_i \right]$$

$$= RT \left[n_1 \ln \gamma_1 + n_2 \ln \gamma_2 - n_1 \ln x_1 - n_2 \ln x_2 \right]$$

$$G^E = RT \left[n_i \ln \gamma_i \right]$$

If we have two component (binary mixture)

$$G^E = RT \left[n_1 \ln \gamma_1 + n_2 \ln \gamma_2 \right]$$

12
Thursday

Mon	Tue	Wed	Thu	Fri	Sat
4	5	6	7	1	2
11	12	13	14	8	9
18	19	20	21	15	16
24	25	26	27	22	23
				29	30

(vi)

③ Excess Entropy.

$$S^E = \left(- \frac{\partial G^E}{\partial T} \right)_P$$

Putting the value of G^E

$$S^E = -RT \left[n_1 \left(\frac{\partial \ln \gamma_1}{\partial T} \right)_P + n_2 \left(\frac{\partial \ln \gamma_2}{\partial T} \right)_P \right]$$

$$= -R \left[n_1 \left(\ln \gamma_1 \frac{\partial T}{\partial T} \right)_P + n_2 \left(\ln \gamma_2 \frac{\partial T}{\partial T} \right)_P \right]$$

$$= -R \left[n_1 \ln \gamma_1 + n_2 \ln \gamma_2 \right]$$

④ Excess Enthalpy. (H^E)

$$H^E = H_{Real}^{mix} - H_{ideal}^{mix}$$

$$H^E = \Delta H_m^E (Real)$$

$$= -RT^2 \left(n_1 \frac{\partial \ln \gamma_1}{\partial T} + n_2 \frac{\partial \ln \gamma_2}{\partial T} \right)$$

(Since $H_{ideal}^{mix} = 0$)

$$H^E = H_{Real}^{mix} - H_{ideal}^{mix} + H^0 - H^0$$

$$= (H^0 + H_{Real}^{mix}) - (H^0 + H_{ideal}^{mix})$$

$$= \Delta H_{Real}^{mix} - \Delta H_{ideal}^{mix}$$

Excess volume

$$V^E = \left(\frac{\partial G^E}{\partial P} \right)_T$$

Putting the value of G^E

$$V^E = RT \left(n_1 \frac{\ln \gamma_1}{\partial P} + n_2 \frac{\ln \gamma_2}{\partial P} \right)$$