Ideal Gas Mixtures

1 Substance Specification

Assume mixture of **m pure substances**, to specify substance, we need **m-1** mole fractions.

Recall the state postulate, for simple compressible substance, we need 2 additional **independent intensive variables** to define a state:

$$I_3 = I_3(I_1, I_2, X_1, \dots, X_{m-1})$$
(1)

To determine any extensive property of the system, we must add **one additional extensive property**:

$$E_J = E_J(E_1, I_1, I_2, X_1, \dots, X_{m-1})$$
⁽²⁾

2 Basic Properties

2.1 Averaged Properties

The molar mass of the mixture could be expressed as:

$$MW_{mix} = \sum_{i} X_i M W_i \tag{3}$$

Where X_i is the mole fraction:

$$X_i = \frac{n_i}{n_{mix}} \tag{4}$$

Then we have the mixture specific gas constant:

$$R_{mix} = \frac{\bar{R}}{MW_{mix}} \tag{5}$$

And the ideal gas law:

$$p = \rho R_{mix} T \tag{6}$$

Similarly, the specific heat could be expressed as:

$$c_{p_{mix}} = \sum_{i} Y_i c_{p_i} \tag{7}$$

Where Y_i is the mass fraction:

$$Y_i = \frac{m_i}{m_{mix}} \tag{8}$$

3 Enthalpy

There are two ways to express the enthalpy of the mixture. Again we assume gas C composed of gases A and B. Firstly, we can use averaged property:

$$\Delta H_{C_{1,2}} = m_{mix} \int_{T_1}^{T_2} c_{p_{mix}} dT$$
(9)

Or we can calculate the enthalpy change of individual gas:

$$\Delta H_{C_{1,2}} = \Delta H_{A_{1,2}} + \Delta H_{B_{1,2}}$$

= $m_A [h_A(T_2) - h_A(T_1)] + m_B [h_B(T_2) - h_B(T_1)]$
= $m_A \int_{T_1}^{T_2} c_{p_A} dT + m_B \int_{T_1}^{T_2} c_{p_B} dT$ (10)

4 Entropy

Similarly with enthalpy, we can use averaged properties to calculate the entropy of mixture:

$$\Delta S_{C_{1,2}} = m_{mix} \left[\int_{T_1}^{T_2} c_{p_{mix}} dT - R_{mix} ln(\frac{p_2}{p_1}) \right]$$
(11)

Or we can use partial pressure to calculate individual entropy change:

$$\Delta S_{C_{1,2}} = m_A \left[\int_{T_1}^{T_2} c_{p_A} dT - R_A ln(\frac{p_{2A}}{p_{1A}}) \right] + m_B \left[\int_{T_1}^{T_2} c_{p_B} dT - R_B ln(\frac{p_{2B}}{p_{1B}}) \right]$$
(12)

Notice that if we mix two ideal gas, the entropy will increase because of diffusion will let the system reach the equilibrium state at the end.

We can also use volume:

$$S_C = S_A(U_A, V_A) + S_B(U_B, V_B)$$
(13)

$$dS_A = \left(\frac{dU}{T}\right)_A + \left(\frac{p}{T}dV\right)_A$$

= $\left(\frac{dU}{T}\right)_A + \left(\frac{pV}{T}\frac{dV}{V}\right)_A$
= $\left(\frac{dU}{T}\right)_A + \left(Nk_B\frac{dV}{V}\right)_A$ (14)

Similarly:

$$dS_B = \left(\frac{dU}{T}\right)_B + \left(Nk_B\frac{dV}{V}\right)_B \tag{15}$$

5 Molar Property

5.1 Molar property

We define molar property as the property of substance per mole of mixture:

$$\hat{u} = \frac{U}{n}, \hat{s} = \frac{S}{n}, \hat{h} = \frac{H}{n}, \hat{v} = \frac{V}{n}$$

$$\tag{16}$$

With this relation, we can get:

$$dU = \hat{u}dn + nd\hat{u} \tag{17}$$

$$dS = \hat{s}dn + nd\hat{s} \tag{18}$$

$$dV = \hat{v}dn + nd\hat{v} \tag{19}$$

Recall that:

$$dU = TdS - pdV + \sum_{i=1}^{k} \mu_i dn_i \tag{20}$$

Therefore:

$$\hat{u}dn + nd\hat{u} = T\hat{s}dn + Tnd\hat{s} - p\hat{v}dn - pnd\hat{v} + \sum_{i=1}^{k} \mu_i dn_i$$
(21)

$$nd\hat{u} = Tnd\hat{s} - pnd\hat{v} + \sum_{i=1}^{k} \mu_i dn_i - (\hat{u} - T\hat{s} + p\hat{v})dn$$
(22)

Recall that:

$$G = H - TS = U + pV - TS \tag{23}$$

Therefore:

$$\hat{g} = G/n = \hat{u} - T\hat{s} + p\hat{v} \tag{24}$$

Using the following relations:

$$n = \sum_{i} n_i, dn = \sum_{i} dn_i, G = \sum_{i} \mu_i n_i$$
(25)

$$n_i = X_i n, dn_i = X_i dn + n dX_i \tag{26}$$

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Finally we have the following expressions:

$$d\hat{u} = Td\hat{s} - pd\hat{v} + \sum_{i} \mu_{i} dX_{i}$$
⁽²⁷⁾

$$d\hat{h} = Td\hat{s} + \hat{v}dp + \sum_{i} \mu_{i}dX_{i}$$
⁽²⁸⁾

$$d\hat{g} = -\hat{s}dT + \hat{v}dp + \sum_{i} \mu_{i}dX_{i}$$
⁽²⁹⁾

If it is single component substance, then we can reduce the chemical potential term.

5.2 Partial Molar Property

A partial molar property is a concept in thermodynamics that provides a measure of the change in a thermodynamic property (e.g., enthalpy, entropy, volume, etc.) of a mixture resulting from the addition of an infinitesimal amount of a component **at constant temperature, pressure, and composition of all other components.** Partial molar properties are used to account for non-ideal behavior in mixtures and are particularly important for understanding solutions. In short, **partial molar property is the property of substance per mole of one species in mixture.**

Let B be any extensive property, then the partial molar version of B is:

$$\bar{b}_i = \frac{\partial B}{\partial n_i}|_{p,T,n_{j\neq i}} \tag{30}$$

We also have:

$$B = \sum_{i} \bar{b}_{i} n_{i} \tag{31}$$

Here \bar{b}_i is B per mole of i in mixture, for given mixture composition. With this definition, we have:

$$\bar{h}_i = \bar{u}_i + p\bar{v}_i \tag{32}$$

$$\bar{g}_i = \bar{h}_i - T\bar{s}_i = \frac{\partial G}{\partial n_i}|_{p,T,n_{j\neq i}} = \mu_i$$
(33)

Using Maxwell Relations, we have:

$$d\bar{g}_i = d\mu_i = \bar{v}_i dp - \bar{s}_i dT + \sum_{i=1}^{m-1} \frac{\partial \mu_i}{\partial X_i} |_{T,p,X_{j\neq i}} dX_i$$
(34)

$$d\bar{u}_i = T_i d\bar{s}_i - p d\bar{v}_i + \sum_{i=1}^{m-1} \frac{\partial \mu_i}{\partial X_i} |_{T,p,X_{j\neq i}} dX_i$$
(35)

$$d\bar{h}_i = T_i d\bar{s}_i + \bar{v}_i dp + \sum_{i=1}^{m-1} \frac{\partial \mu_i}{\partial X_i} |_{T,p,X_{j\neq i}} dX_i$$
(36)

6 Mixing Process (Using Chemical Potential)

6.1 Pure substance

In previous chapter, we already introduce the definition of chemical potential. Now we want to use this property to analyze the TD problem. First we define:

$$\mu = \mu(p, T) \tag{37}$$

Then we assume at same T:

$$\mu^{o} = \mu(p^{o}, T) = \mu^{o}(T)$$
(38)

Here μ^{o} is the standard chemical potential at reference pressure p^{o} , which is function of only T.

Under TPG assumption:

$$\mu = \mu^o(T) + \bar{R}T \ln \frac{p}{p^o} \tag{39}$$

Normally we set p^o as 1 unit, so we have:

$$\mu = \mu^o(T) + \bar{R}T\ln p \tag{40}$$

6.2 Perfect Gas Mixtures

Now we define μ_i and μ_i^o as the chemical potentials of i^{th} component of gas, having mole fraction X_i . Therefore, for TPG mixture:

$$\mu_{i} = \mu_{i}^{o}(T) + \bar{R}T \ln \frac{p}{p^{o}} + \bar{R}T \ln X_{i}$$
(41)

The first two terms are independent of composition, and the last term depends on composition.

Now we introduce a property, called **partial pressure**. Partial pressure is a concept used in thermodynamics and chemistry to describe the pressure that a single gas component in a mixture of gases would exert if it occupied the entire volume of the container by itself, while keeping the temperature constant. The expression is:

$$p_i = pX_i \tag{42}$$

If we again assume reference pressure as 1 unit, then we have:

$$\mu_i = \mu_i^o(T) + \bar{R}T \ln(pX_i) = \mu_i^o(T) + \bar{R}T \ln p_i$$
(43)

Some remarks:

1.

$$\mu_i = \mu_i(p_i, T) = \hat{g}_i(p_i, T) \tag{44}$$

So μ_i represents the Gibbs value for pure component i evaluated at p_i and T.

2. μ_i is not a function of $X_{j\neq i}$, so it is independent of other components in mixtures. This decoupling of composition dependence is property of general class of mixtures called Mixtures of Independent Substances.

6.3 State Equations

6.3.1 Ideal Gas Law

With the definitions of partial properties, we can have some new versions of ideal gas law. For component i:

$$\bar{v}_i = \frac{\partial \mu_i}{\partial p}|_{T,X_j} = \frac{\bar{R}T}{p} \tag{45}$$

$$p\bar{v}_i = \bar{R}T\tag{46}$$

For mixture:

$$pV = mRT, \ p\frac{V}{n} = \frac{m}{n}RT, \ p\hat{v} = \bar{R}T$$
 (47)

So we can get $\bar{v}_i = \hat{v}$, so for the ideal gas, molar volume same for components in mixture.

Using partial pressure:

$$p_i = X_i p = X_i \frac{\bar{R}T}{V/n} = \frac{X_i n \bar{R}T}{V}$$
(48)

$$p_i V = n_i \bar{R} T \tag{49}$$

6.3.2 Enthalpy

Recall that:

$$\mu_i = \bar{g}_i = \bar{h}_i - T\bar{s}_i \tag{50}$$

Based on the Maxwell relation, we have:

$$\bar{s}_i = \frac{\partial S}{\partial n_i}|_{T,p,n_{j\neq i}} = -\frac{\partial \mu_i}{\partial T}|_{p,X_j,X_i}$$
(51)

Therefore:

$$\mu_i = \bar{h}_i + T \frac{\partial \mu_i}{\partial T}|_{p, X_j, X_i}$$
(52)

$$\frac{h_i}{T^2} = \frac{\mu_i}{T^2} - \frac{1}{T} \frac{\partial \mu_i}{\partial T} = -\frac{\partial (\mu_i/T)}{\partial T}$$
(53)

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Then for the TPG mixture:

$$\mu_i = \mu_i^o + \bar{R}T\ln p + \bar{R}T\ln X_i \tag{54}$$

Divide by T and then take the derivative of T:

$$\frac{\partial(\mu_i/T)}{\partial T} = \frac{d}{dT} \left(\frac{\mu_i^o}{T}\right) \tag{55}$$

Now recall that:

$$\mu = \frac{G}{n} = \hat{g} = \hat{h} - T\hat{s} \tag{56}$$

Therefore:

$$\hat{h} = \mu + T\hat{s} \tag{57}$$

For the mixture we have (now independent of composition!):

$$\hat{s} = -\frac{\partial\mu}{\partial T}\Big|_p = -\frac{d\mu^o}{dT} - \bar{R}\ln p \tag{58}$$

And:

$$\mu = \mu^o + \bar{R}T\ln p \tag{59}$$

So:

$$\hat{h} = \mu^{o} + \bar{R}T \ln p - T(\frac{d\mu^{o}}{dT} + \bar{R}\ln p) = \mu^{o} - T\frac{d\mu^{o}}{dT}$$
(60)

Therefore:

$$\frac{\hat{h}_i}{T^2} = \frac{\mu^o}{T^2} - \frac{1}{T} \frac{d\mu^o}{dT} = -\frac{d}{dT} (\frac{\mu_i^o}{T})$$
(61)

Finally we have:

$$\frac{\hat{h}_i}{T^2} = \frac{\bar{h}_i}{T^2} \tag{62}$$

$$\hat{h}_i(T) = \bar{h}_i(T) \tag{63}$$

Similarly:

$$\hat{u}_i(T) = \bar{u}_i(T) \tag{64}$$

Then we have:

$$H(T) = \underbrace{\sum_{i} n_{i} \bar{h}_{i}(T)}_{\text{mixed gases}} = \underbrace{\sum_{i} n_{i} \hat{h}_{i}(T)}_{\text{unmixed gases}}$$
(65)

Conclusion: There is no ΔH or ΔU due to mixing!

6.3.3 Entropy

Start from Gibbs energy, for TPG mixture:

$$G = \sum_{i} n_i \bar{g}_i = \sum_{i} n_i (\mu_i^o + \bar{R}T \ln p_i) \tag{66}$$

Here, we define p^i as the pressure of i^{th} component before mixed, and μ^i is the chemical potential of i^{th} component before mixed. Therefore:

$$\mu^i = \mu^o_i + \bar{R}T \ln p^i \tag{67}$$

$$G = \sum_{i} n_i (\mu^i + \bar{R}T \ln \frac{p_i}{p^i}) \tag{68}$$

Therefore:

$$\Delta G_{mixing} = \bar{R}T \sum_{i} n_i \ln \frac{p_i}{p^i} \tag{69}$$

Recall that when T is constant:

$$\Delta G_{mixing} = \Delta H_{mixing} - T\Delta S_{mixing} \tag{70}$$

From previous section, we know there will be no enthalpy change during mixing, so $\Delta H_{mixing} = 0$. Then:

$$\frac{\Delta G_{mixing}}{T} = -\Delta S_{mixing} = \bar{R} \sum_{i} n_i \ln \frac{p_i}{p^i}$$
(71)

Is it possible to have isentropic mixing for 2 gases? Yes! At this case, final partial pressures must be same as initial pressures. This requires isothermal and reversible compression, so work in and heat transfer out.

Two special cases in summary:

1. All gases have same initial pressures, which also match final pressure $(p^i = p_i)$, then:

$$\frac{\Delta G_{mixing}}{T} = -\Delta S_{mixing} = \bar{R} \sum_{i} n_i \ln \frac{pX_i}{p^i} = \bar{R} \sum_{i} n_i \ln X_i < 0 \quad (72)$$

So this mixing produces entropy as expected.

2. Initial pressure of each gas is same as its final partial pressure in the mixture $(p_i = p^i)$ for each i:

$$\frac{\Delta G_{mixing}}{T} = -\Delta S_{mixing} = \bar{R} \sum_{i} n_i \ln \frac{p_i}{p^i} = 0$$
(73)

In this case no entropy change, but requires work and heat transfer.