GOOD NEWS!

5/30 1 lecture to go!

6/1   Last day of the THERMO 004!

6/6(화) Holiday

6/5 문제풀이세션 (시간 미정)

6/13(목) 시험시간 8:30-9:30

- Last Homework (due 6/13)

    10-1, 3, 6, 10

    11-8, 24

    12-2, 4, 7, 11, 31, 45

Chapter 11 Thermodynamic Relations

Thus far, we have talked about several thermodynamic properties.

$p,\ v,\ \rho,\ T,\ m,\ e,\ h,\ s,\ c_p,\ c_v \ldots$

F (Helmholtz free energy), f (per unit mass)
G (Gibbs' free energy), g

Two Important Relations

Consider a variable z that is a continuous function of x and y.

$$z = f(x, y)$$

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

It is convenient to rewrite this as

$$dz = M\ dx + N\ dy \quad \text{--------------------}(*)$$

The physical significance of the partial derivatives can be understood from p v T diagram (surface) of the superheated vapor.

(x, y, z)   (p, v, T)

e.g. Evaluate the partial derivatives along a constant-temperature line,

$\frac{p}{v}\ _T$

In (*), if x, y and z are all point functions (i.e. quantities that depend only on the state and are independent of the path) the differentials are exact differentials. That is

$$\frac{M}{y}\ _x \qquad \frac{N}{x}\ _y \quad \text{------------------------}(1)$$

The second important relations follow. Consider

x f (y , z)

and dx x/y |z dy x/z |y dz (a)

Similarly, y f (x , z) then

dy y/x z dx y/z x dz (b)

Sub (b) (a) we have

dx x/y z y/x |z dx y/z |x dz x/z |y dz

x/y |z y/x |z dx x/y |z y/z |x x/z |y dz

Two possible cases.

If $dz = 0,\ dx \neq 0$, then

$$\left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial x}\right|_z = 1$$

If $dx = 0,\ dz \neq 0$, then

$$\left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial z}\right|_x + \left.\frac{\partial x}{\partial z}\right|_y = 0$$

or

$$\left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial z}\right|_x \left.\frac{\partial z}{\partial x}\right|_y = -1 \qquad \text{--------------------(2)}$$

2 개의 성질을 알고 제 3의 성질을 구할 때 쓴다.

- Maxwell Relations

  Four equations relating the properties p, v, T, s

  Recall what we already derived,

$$du = T\,ds - p\,dv \qquad (3)$$

$$dh = T\,ds + v\,dp \qquad (h = u + pv) \qquad (4)$$

The remaining two are derived from the definition of the Helmholtz function, f.

$$f = u - Ts$$

$$so\ df = du - T\,ds - s\,dT$$

Sub (3) into above

$$df = -p\,dv - s\,dT \qquad (5)$$

Similarly, using Gibb's energy

$$g = h - Ts$$

$$dg = dh - T\,ds - s\,dT$$

Sub (4) into above gives

$$dg = v\,dp - s\,dT \qquad (6)$$

Since eqns (3), (4), (5), (6) are relations involving properties, we conclude that these are exact differentials and thus, are of the general form.

$$dz = M\,dx + N\,dy$$

Since $\left.\dfrac{\partial M}{\partial y}\right|_x = \left.\dfrac{\partial N}{\partial s}\right|_v$

From (3) we have

$$\left.\frac{\partial T}{\partial v}\right|_s = -\left.\frac{\partial p}{\partial s}\right|_v$$

From (4) we have

$$\left.\frac{\partial T}{\partial p}\right|_s = \left.\frac{\partial v}{\partial s}\right|_p$$

From (5) we have

$$\left.\frac{\partial p}{\partial T}\right|_v = \left.\frac{\partial s}{\partial v}\right|_T$$

From (6) we have

$$\left.\frac{\partial v}{\partial T}\right|_p = -\left.\frac{\partial s}{\partial p}\right|_T$$

Maxwell's relations for simple compressible system

- Note p, T, v can be measured experimentally but s cannot be measured experimentally.
- By using the Maxwell Relations, we can determine changes in entropy from quantities that can be measured, (i.e. p, T, v).
- There are some additional useful relations from (3) -> (6)

$$\left.\frac{\partial u}{\partial s}\right|_v = T, \quad \left.\frac{\partial u}{\partial v}\right|_s = -p$$

$$\left.\frac{\partial h}{\partial s}\right|_p = T, \quad \left.\frac{\partial h}{\partial p}\right|_s = v$$

$$\left.\frac{\partial f}{\partial v}\right|_T = -p, \quad \left.\frac{\partial f}{\partial T}\right|_v = -s$$

$$\left.\frac{\partial g}{\partial p}\right|_T = v, \quad \left.\frac{\partial g}{\partial T}\right|_p = -s$$

Chapter 12 Mixtures

Air consisting of N_2, O_2, etc
Though we've assumed it a non-mixture.

Mass fraction $f_i = \frac{m_i}{m}$

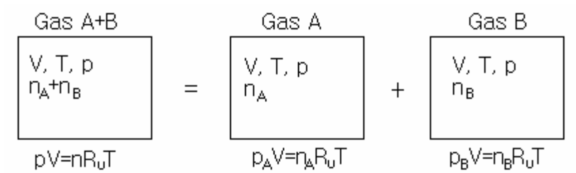
$$\sum_k f_i = 1$$

Number of moles, $n_1, n_2, ..n_i, ...n_k$

Mole fraction $x_i = \frac{n_i}{n}$

$$\sum_k x_i = 1$$

Dalton Model (V, T same)

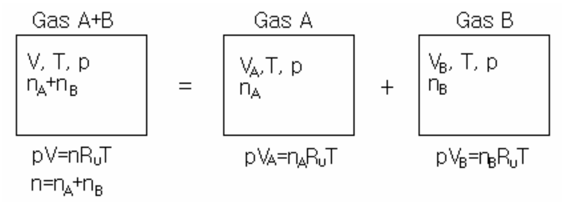


$$\frac{p_A}{p} = \frac{n_A}{n} = x_A$$; p_A = partial pressure of component A

$$\frac{p_B}{p} = \frac{n_B}{n} = x_B$$; p_B = partial pressure of component B

$$p_A + p_B = p$$ = total pressure

Amagat Model (p, T same)



$$\frac{V_A}{V} = \frac{n_A}{n} = x_A$$; V_A = partial volume of component A

$$\frac{V_B}{V} = \frac{n_B}{n} = x_B$$; V_B = partial volume of component B

$$V_A + V_B = V$$ = total volume

$$\therefore \frac{V_A}{V} + \frac{V_B}{V} = 1$$

In general,

$$\frac{p_i}{p} = \frac{V_i}{V} = \frac{n_i}{n} = x_i$$

and

$$\sum_k p_i = p, \qquad \sum_k V_i = V$$

- 혼합기체 n 몰의 질량, m
- 성분 i 의 질량, m_i
- 분자량 (molecular weight), M_i
- 상당 분자량 M

$$n_i = \frac{m_i}{M_i} \qquad \frac{kg}{kg/kmol} = kmol$$

$$n = \frac{m}{M}$$

$$\therefore M = \frac{m}{n} = \frac{\sum_k n_i M_i}{n} = \sum_k x_i M_i \ \frac{kg}{kmol}$$

$$n = \sum_k n_i$$

$$\frac{m}{M} = \sum_k \frac{m_i}{M_i}$$

or

$$M = \left(\sum_k \frac{f_i}{M_i} \right)^{-1}$$

Molecular weight for the mixture
(혼합기체에 대하여 상당분자량을 정의하여 순수기체와 같이 취급할 수 있다)

순수공기

		Mole Fraction	Molec. Weight	Mass per kmol of mixture	Mass Fraction
	% Volume	x_i	M_i	$x_i M_i$	$f_i = \frac{x_i M_i}{M}$
N_2	78.03	0.7803	28.016	21.861	0.7547
O_2	20.99	0.2099	32.00	6.717	0.2319
Ar	0.94	0.0094	39.944	0.376	0.0130
CO_2	0.03	0.0003	44.003	0.013	0.0004
H_2	0.01	0.0001	2.016	–	–
Sum	100	1		$M = 28.967 = \sum x_i M_i$	1

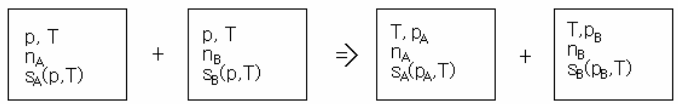
Molec. Wt for mixture

For the mixture

$$R = \frac{R_u}{M} = \frac{8.314}{28.967} \frac{kJ/kmol.K}{kg/kmol} = 0.287 \ kJ/kg.K$$

이상기체 혼합물의 엔트로피

$$\left.\begin{matrix} Gases\ A, n_A 몰, p, T \\ Gases\ B, n_B 몰, p, T \end{matrix}\right\} \quad \text{Mix} \to \quad p, T$$



Before mixing,

$$\bar{s}_A(p,T) = \int_{T_0}^{T} \bar{c}_{p_A} \frac{dT}{T} - R_u \ln \frac{p}{p_0} + \bar{s}_{0A}$$

$$\bar{s}_B(p,T) = \int_{T_0}^{T} \bar{c}_{p_B} \frac{dT}{T} - R_u \ln \frac{p}{p_0} + \bar{s}_{0B}$$

$$Total\ S = n_A \bar{s}_A(p,T) + n_B \bar{s}_B(p,T)$$