# ME 209
# Basic Thermodynamics
# Property Relations

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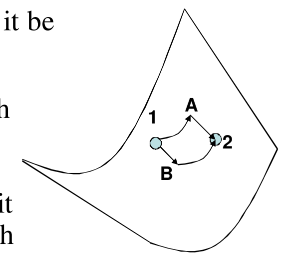
## Concept of Exact Differential-I

- Consider a property surface. Let it be a p,v,T surface
- Let point 1 and 2 be close to each other and the point 1-2 can be reached by infinite number of paths. If we look at dv = $V_2$-$V_1$, it should be independent of the path




- Let 1-A and B-2 be isotherms and 1-B and A-2 be isobars

$$dv_{1-2} = \left.\frac{\partial v}{\partial p}\right|_{T1} dp + \left.\frac{\partial v}{\partial T}\right|_{p2} dT = \left.\frac{\partial v}{\partial T}\right|_{p1} dT + \left.\frac{\partial v}{\partial p}\right|_{T2} dp$$

**Path 1-A-2** **Path 1-B-2**

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## Concept of Exact Differential-II

$$dv_{1-2} = \left.\frac{\partial v}{\partial p}\right|_{T1} dp + \left.\frac{\partial v}{\partial T}\right|_{p2} dT = \left.\frac{\partial v}{\partial T}\right|_{p1} dT + \left.\frac{\partial v}{\partial p}\right|_{T2} dp$$

$$\left(\left.\frac{\partial v}{\partial p}\right|_{T1} dp + \left.\frac{\partial v}{\partial T}\right|_{p2} dT\right) - \left(\left.\frac{\partial v}{\partial T}\right|_{p1} dT + \left.\frac{\partial v}{\partial p}\right|_{T2} dp\right) = 0$$

$$\Rightarrow \left(\left.\frac{\partial v}{\partial p}\right|_{T2} - \left.\frac{\partial v}{\partial p}\right|_{T1}\right) dp = \left(\left.\frac{\partial v}{\partial T}\right|_{p2} - \left.\frac{\partial v}{\partial T}\right|_{p1}\right) dT$$

$$\Rightarrow \frac{\left(\left.\frac{\partial v}{\partial p}\right|_{T2} - \left.\frac{\partial v}{\partial p}\right|_{T1}\right)}{dT} = \frac{\left(\left.\frac{\partial v}{\partial T}\right|_{p2} - \left.\frac{\partial v}{\partial T}\right|_{p1}\right)}{dp}$$

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## Concept of Exact Differential-III

- As the points are close by, we can write the previous equation as

$$\Rightarrow \frac{\partial}{\partial T}\left(\left.\frac{\partial v}{\partial p}\right|_T\right)_p = \frac{\partial}{\partial p}\left(\left.\frac{\partial v}{\partial T}\right|_p\right)_T$$

$$\Rightarrow \frac{\partial^2 v}{\partial T \partial p} = \frac{\partial^2 v}{\partial p \partial T}$$

- The value of a mixed differential is independent of the order of differentiation
- The result is a consequence of assuming dv is independent of direction. Those differentials that satisfy this property are called exact differentials

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## Concept of Exact Differential-IV

- Every property change is an exact differential and Every exact differential represents change of a property
- The whole thing can be generalised as, given three variables x, y and z and they have a relation of the form

$$dz = M(x,y)dx + N(x,y)dy$$

then the differential dz is exact, if

$$\Rightarrow \frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}$$

- In thermodynamics, knowing that properties are exact, we shall equate the cross derivatives

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## Rules of Partial Derivatives-I

- Now let us look at the relation between partial derivatives

$$dx = \left.\frac{\partial x}{\partial y}\right|_z dy + \left.\frac{\partial x}{\partial z}\right|_y dz$$

- Similarly, we can write

$$dy = \left.\frac{\partial y}{\partial x}\right|_z dx + \left.\frac{\partial y}{\partial z}\right|_x dz$$

- Substituting the expression for dy in second equation into the first equation, we get

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

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## Rules of Partial Derivatives-II

- Collecting the coefficients of dx and dz, we can write

$$dx\left(1 - \left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial x}\right|_z\right) = \left(\left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial z}\right|_x + \left.\frac{\partial x}{\partial z}\right|_y\right) dz$$

- Now if we go to two neighboring states such that dz = 0 and dx ≠ 0, then it is necessary to have

$$1 - \left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial x}\right|_z = 0 \qquad \text{Or} \quad \left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial x}\right|_z = 1 \qquad \text{Or} \quad \left.\frac{\partial x}{\partial y}\right|_z = \frac{1}{\left.\frac{\partial y}{\partial x}\right|_z}$$

- We can call the above as Reciprocal Rule

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## Rules of Partial Derivatives-III

- Now if we go to two neighboring states such that dx = 0 and dz ≠ 0, then, we can write,

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

- Now applying the reciprocal rule, we can write

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

- The above can be called as Cyclic Rule

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# Thermodynamic Functions-I

- Having laid the foundation for deriving property relations, we shall now go on to define two new thermodynamic functions called Helmholtz and Gibbs functions
- The Helmholtz function A and Gibbs function G are defined as

$$A = U - TS \qquad G = H - TS$$

- Their intensive counterparts are **a** and **g**

$$a = u - Ts \qquad g = h - Ts$$

- Now we shall begin manipulating these functions

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# Thermodynamic Functions-II

- Let us begin with the two Tds relations that we have derived earlier

$$du = Tds - pdv \quad (1) \qquad dh = Tds + vdp \quad (2)$$

- Differentiating the two functions defined in previous slide, we can write

$$da = du - Tds - sdT \quad (3) \qquad dg = dh - Tds - sdT \quad (4)$$

- Substituting for du-Tds from Eq. (1) in Eq. (3) and similarly substituting for dh-Tds from Eq. (2) in Eq. (4), we get

$$da = -pdv - sdT \quad (5) \qquad dg = vdp - sdT \quad (6)$$

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# Thermodynamic Functions-III

- Now let us manipulate Eq. (1), where u = u(s,v)

$$du = Tds - pdv$$

- Chain rule implies

$$du = \left.\frac{\partial u}{\partial s}\right|_v ds + \left.\frac{\partial u}{\partial v}\right|_s dv$$

- Comparing the above two equations, we can write,

$$\left.\frac{\partial u}{\partial s}\right|_v = T, \quad \left.\frac{\partial u}{\partial v}\right|_s = -p \qquad (7)$$

- From Eq. (2) $dh = Tds + vdp$
- We can write, $\left.\frac{\partial h}{\partial s}\right|_p = T, \quad \left.\frac{\partial h}{\partial p}\right|_s = v \qquad (8)$

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# Thermodynamic Functions-IV

- From Eq. (5) $da = -pdv - sdT$
- We can write, $\left.\frac{\partial a}{\partial v}\right|_T = -p, \quad \left.\frac{\partial a}{\partial T}\right|_v = -s \qquad (9)$
- From Eq. (6) $dg = vdp - sdT$
- We can write, $\left.\frac{\partial g}{\partial p}\right|_T = v, \quad \left.\frac{\partial g}{\partial T}\right|_p = -s \qquad (10)$
- Thus we have obtained the basic thermodynamic properties, p,v,T and s have been defined as the derivative of u, h, a and g. Due to this aspect, u, h, a and g are also called **thermodynamic potentials**

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# Maxwell Relations

- Now we shall use the exact differential rule and relate the derivatives

$$du = Tds - pdv \qquad \Rightarrow \left.\frac{\partial T}{\partial v}\right|_s = -\left.\frac{\partial p}{\partial s}\right|_v \qquad (11)$$

$$dh = Tds + vdp \qquad \Rightarrow \left.\frac{\partial T}{\partial p}\right|_s = \left.\frac{\partial v}{\partial s}\right|_p \qquad (12)$$

$$da = -pdv - sdT \qquad \Rightarrow \left.\frac{\partial p}{\partial T}\right|_v = \left.\frac{\partial s}{\partial v}\right|_T \qquad (13)$$

$$dg = vdp - sdT \qquad \Rightarrow \left.\frac{\partial v}{\partial T}\right|_p = -\left.\frac{\partial s}{\partial p}\right|_T \qquad (14)$$

- The relations in Eqs. (11) – (14) are called Maxwell Relations

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# Auxiliary Relations-I

- Now we shall equate T is Eqs. (7) and (8) to give

$$\Rightarrow \left.\frac{\partial u}{\partial s}\right|_v = \left.\frac{\partial h}{\partial s}\right|_p \qquad (15)$$

- Similarly equating -p is Eqs. (7) and (9) to give

$$\Rightarrow \left.\frac{\partial u}{\partial v}\right|_s = -\left.\frac{\partial a}{\partial v}\right|_T \qquad (16)$$

- Equating v is Eqs. (8) and (10) to give

$$\Rightarrow \left.\frac{\partial h}{\partial p}\right|_s = \left.\frac{\partial g}{\partial p}\right|_T \qquad (17)$$

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# Auxiliary Relations-II

- Equating -s is Eqs. (8) and (10) to give

$$\Rightarrow \left.\frac{\partial a}{\partial T}\right|_v = \left.\frac{\partial g}{\partial T}\right|_p \qquad (18)$$

- The fundamental question that arises is what is the use of all these relations?
- They provide means to construct property tables from the measured p, v and T data and some additional measurements
- The aim is to measure minimum quantities and construct property data