Slide 1/17

ME 209
Basic Thermodynamics
Property Relations

Kannan Iyer
Kiyer@me.iitb.ac.in

Department of Mechanical Engineering
Indian Institute of Technology, Bombay

Slide 2/17

Application-I

- Let us explore as to how an enthalpy table can be constructed for water that has a complex behaviour when both liquid and vapour phases have to be addressed

$$h(T,p) \Rightarrow dh = \left.\frac{\partial h}{\partial T}\right|_p dT + \left.\frac{\partial h}{\partial p}\right|_T dp$$

- The equation that connects dh and dp is

$$dh = Tds + vdp$$

- As we need the derivative of h with p along constant T, we can manipulate the previous equation and write,

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

Maxwell Relation Eq. (13)

Slide 3/17

Application-II

- Thus, we can write

$$\Rightarrow dh = c_p dT + \left(v - T\left.\frac{\partial v}{\partial T}\right|_p\right)dp \qquad (19)$$

- Thus, along an isobar,

$$\Rightarrow dh_p = c_p dT_p$$

- Now, if we move along isotherm, we can write

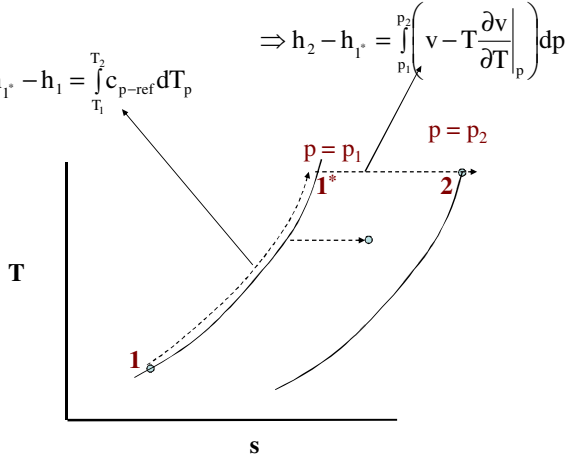$$\Rightarrow dh_T = \left(v - T\left.\frac{\partial v}{\partial T}\right|_p\right)dp_T$$

- For finding the change in enthalpy, we need c_p variation with T at one convenient pressure and $v(p,T)$

Slide 4/17

Application-III

$$\Rightarrow h_2 - h_{1^*} = \int_{p_1}^{p_2}\left(v - T\left.\frac{\partial v}{\partial T}\right|_p\right)dp$$

$$\Rightarrow h_{1^*} - h_1 = \int_{T_1}^{T_2} c_{p-ref} dT_p$$

$p = p_1$ $p = p_2$

1*   2

T

1

s

Thus for any single-phase region we can use this concept

Application-IV

- We had shown that

$$\Rightarrow dh = c_p dT + \left(v - T \frac{\partial v}{\partial T}\bigg|_p \right) dp$$

- If we had ideal gas, then

$$v = \frac{RT}{p} \qquad \Rightarrow \frac{\partial v}{\partial T}\bigg|_p = \frac{R}{p} \qquad \Rightarrow T\frac{\partial v}{\partial T}\bigg|_p = \frac{RT}{p} = v$$

$$\therefore dh = c_p dT$$

- Thus, h only varies with temperature and is independent of pressure

Relation Between c_p and Entropy

- From the Tds relation,

$$dh = Tds + vdp$$

$$= T\left(\frac{\partial s}{\partial T}\bigg|_p dT + \frac{\partial s}{\partial p}\bigg|_T dp \right) + vdp$$

$$= T\frac{\partial s}{\partial T}\bigg|_p dT + \left(T\frac{\partial s}{\partial p}\bigg|_T + v \right) dp$$

- Also,

$$dh = \frac{\partial h}{\partial T}\bigg|_p dT + \frac{\partial h}{\partial p}\bigg|_T dp$$

$$\Rightarrow T\frac{\partial s}{\partial T}\bigg|_p = c_p, \quad \frac{\partial h}{\partial p}\bigg|_T = \left(T\frac{\partial s}{\partial p}\bigg|_T + v \right)$$

Evaluation of Entropy Change

- Now we shall derive the relationship for change in entropy

$$s(T,p) \quad \Rightarrow ds = \frac{\partial s}{\partial T}\bigg|_p dT + \frac{\partial s}{\partial p}\bigg|_T dp$$

From previous slide ← → **From Maxwell Relation Eq. (14)**

$$= \frac{c_p}{T} dT + \left(-\frac{\partial v}{\partial T}\bigg|_p dp \right)$$

- The change in entropy can be obtained just as we got change in enthalpy by using pvT relation and c_p as a function of T at one reference pressure.

- For ideal gas, it is fairly straight forward to show that

$$ds = \frac{c_p}{T} dT - \frac{R}{p} dp$$

Properties with Phase Change-I

- We have shown how thermodynamic properties (h,s) can be computed for a fluid, from a reference datum, by knowing the pvT relation and c_p as a function of T at a reference pressure

- From our previous chapters, we have recognised that in phase change region, there is degeneracy between p and T as one depends on the other.

- This leads to the following

$$\frac{\partial T}{\partial p}\bigg|_s = \frac{\partial v}{\partial s}\bigg|_p \quad \text{Maxwell Relation Eq. (12)} \qquad \Rightarrow \frac{\partial p}{\partial T}\bigg|_s = \frac{s_{fg}}{v_{fg}} \quad \text{Using Reciprocal Rule}$$

$$\frac{\partial p}{\partial T}\bigg|_v = \frac{\partial s}{\partial v}\bigg|_T \quad \text{Maxwell Relation Eq. (13)} \qquad \Rightarrow \frac{\partial p}{\partial T}\bigg|_v = \frac{s_{fg}}{v_{fg}}$$

Slide 9/17

Properties with Phase Change-II

- Thus we have shown that the variation of saturated pressure with temperature is independent of at least two paths. Being a simple substance, two independent path having no effect can be generalised to the statement

$$\Rightarrow \left.\frac{\partial p}{\partial T}\right|_{any-process-2phase} = \left.\frac{dp}{dT}\right|_{sat} = \frac{s_{fg}}{v_{fg}} \quad \text{(20)}$$

- Using Tds relation along the constant pressure line

$$dh = Tds + v\cancel{dp} \qquad \Rightarrow h_{fg} = Ts_{fg} \quad \text{(21)}$$

- Eqs. (20) and (21) lead to

$$= \left.\frac{dp}{dT}\right|_{sat} = \frac{h_{fg}}{Tv_{fg}} \quad \text{(22)} \qquad \text{Clapeyron Equation}$$

Slide 10/17

Properties with Phase Change-III

- At low pressures, this can be simplified as follows

$$\Rightarrow \left.\frac{dp}{dT}\right|_{sat} = \frac{h_{fg}}{T\left(v_g - \cancel{v_f}\right)} = \frac{h_{fg}}{T\frac{RT}{p}} = \frac{h_{fg}p}{RT^2}$$

Relatively negligible   **p Assumed as ideal gas**

$$\Rightarrow \left.\frac{d\ln(p)}{dT}\right|_{sat} = \frac{h_{fg}}{RT^2} \quad \text{(23)} \qquad \text{Clausius-Clapeyron Equation}$$

- If h_{fg} can be fitted as a function of T, then the above equation can be analytically integrated to get an expression for $\ln(p)$

$$\Rightarrow \ln\left.\frac{p_{sat}}{p_{sat-Ref}}\right| = \int_{T_{Sat-Ref}}^{T_{Sat}} \frac{h_{fg}(T)}{RT^2} dT$$

Slide 11/17

Properties with Phase Change-IV

- Now we can bridge the two ends of saturated region and construct the variation of h and s in the whole of state space from a given reference point.

- We had already seen the procedure to compute h and s between any two points in single-phase phase using c_p at a reference pressure and the pvT relation in the state space

- From the pvT relation, at any given T on the two-phase dome, we should be able to estimate h_g-h_f with known $\left.\frac{dp}{dT}\right|_{sat}$ and v_{fg} by using Eq. (22) and s_g-s_f using Eq. (21)

- The procedure to estimate is graphically now demonstrated in the next slide

Slide 12/17

- To get properties (h,s) at 2, we use the route 1-1*-2*-2
- To get properties (h,s) at 3, we can use the route 1-s - 3 or 1-1*-2*-3*-3**-3***-3
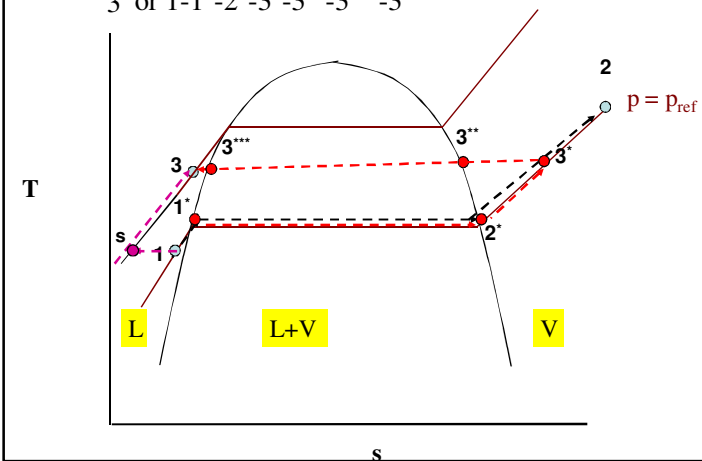
Other Thermodynamic Properties-I

- There are several other themodynamic properties that are used in different fields. These are just introduced here for the sake of completeness

Volume Expansivity

$$\beta = \frac{1}{v}\frac{\partial v}{\partial T}\bigg|_p$$

Isothermal Compressibility

$$\kappa = -\frac{1}{v}\frac{\partial v}{\partial p}\bigg|_T$$

Other Thermodynamic Properties-II

Isentropic Compressibility

$$\alpha = -\frac{1}{v}\frac{\partial v}{\partial p}\bigg|_s$$

- We will show in compressible fluid flow that

$$c^2 = \frac{\partial p}{\partial \rho}\bigg|_s = -v^2\frac{\partial p}{\partial v}\bigg|_s$$

- This implies that

$$c^2\alpha = v \implies \alpha = \frac{v}{c^2}$$

This can be experimentally estimated by measuring v and c

Other Thermodynamic Properties-III

Joule-Thompson Coefficient

$$\mu = -\frac{\partial T}{\partial p}\bigg|_h$$

- This property can also be experimentally measured by conducting a porous plug experiment

P_1, T_1 P_2, T_2

- The valve controls the flow and hence the pressure drop
- If there is no work and heat interaction and if kinetic and potential effects are negligible, the process is Isenthalpic

Other Thermodynamic Properties-IV

- For a given initial pressure and temperature, the exit pressure can be adjusted by adjusting the valve and exit temperature can be measured.
- The slope of the curve obtained is the Joule-Thompson Coefficient
- It can be positive, negative or zero
- The value at which the slope is zero is called inversion point

T

- If the initial state is to the left of inversion point, the gas will cool on expansion

p
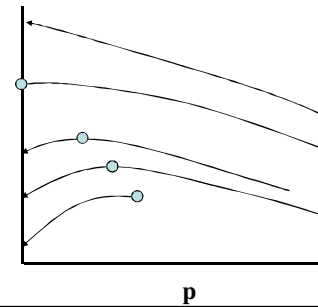
17/17

Computerised Steam Tables

- While in principle, the previously described methods can be used, the newer computerised steam tables follow a different approach

- They fit an equation for Helmholtz function a (ρ,T) and the constants are optimised using experimental data pvT and other parameters such as speed of sound, Joule-Thompson coefficient, etc.

- The properties can then be extracted using the following definitions

$$p = -\rho^2 \left.\frac{\partial a}{\partial \rho}\right|_T \qquad s = -\left.\frac{\partial a}{\partial T}\right|_\rho \qquad u = a + Ts \qquad h = u + p/\rho$$