

## Lecture 6 Putting potentials to work ①

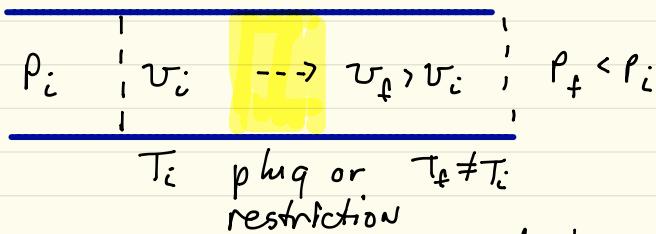
Already discussed how potentials can be used to determine heat/work associated with various processes and to locate equilibria

We'll do lots of this

### Two issues

- often we are interested in processes that don't map directly to one of our potentials
- sometimes we only know susceptibilities

## Joule-Thomson effect as an example



reversible? NO  
quasi-static?

Adiabatic pressure drop across plug .

Slug of gas has initial energy  $u_i$  and final energy  $u_f$ . Work done on slug is

$$W = - (P_f v_f - P_i v_i)$$

On left side compressed from  $v_i \rightarrow 0$ ,

$$W_i = -P_i (-v_i)$$

On right side expanded from  $0 \rightarrow v_f$

$$W_f = -P_f (v_f - 0)$$

$$U_f = U_i + W_i + W_f$$

Energy conservation tells us

$$U_f = U_i + W \quad (\text{adiabatic})$$

$$= U_i + P_i v_i - P_f v_f$$

$$U_f + P_f v_f = U_i + P_i v_i \rightarrow$$

$$H_f = H_i$$

## I senthalpic expansion

What is change in temperature? If small enough to be treated as differential, what is  $\left(\frac{\partial T}{\partial P}\right)_{H, n}$ ?

Pull out our thermodynamic relationships!!

If held constant — no Maxwell relation will help us... yet.

(4)

Recall relation  $(\frac{\partial X}{\partial Y})_Z = -(\frac{\partial Z}{\partial Y})_X (\frac{\partial X}{\partial Z})_Y$

$$dZ = \left(\frac{\partial Z}{\partial X}\right)_Y dX + \left(\frac{\partial Z}{\partial Y}\right)_X dY \quad dZ=0$$

Can use to relate ~~boring potential~~ out

$$\left(\frac{\partial T}{\partial P}\right)_{H,N} = - \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial T}{\partial H}\right)_P \quad \text{drop the } N$$

$$\left(\frac{\partial T}{\partial H}\right)_P = 1 / \left(\frac{\partial H}{\partial T}\right)_P = 1 / N C_P \quad \text{easy}$$

$$\left(\frac{\partial H}{\partial P}\right)_T \dots \quad dH = T dS + V dP \quad \text{constant } N$$

$$\left(\frac{\partial H}{\partial P}\right)_T = T \left(\frac{\partial S}{\partial P}\right)_T + V \quad \text{still messy}$$

$$\left(\frac{\partial S}{\partial P}\right)_T ? \quad \text{Maxwell relation from Gibbs potential}$$

$$\left(\frac{\partial S}{\partial P}\right)_T = - \left(\frac{\partial U}{\partial T}\right)_{P,N} = -U\alpha$$

$$\left(\frac{\partial U}{\partial P}\right)_T = -TV\alpha + V = V(1-T\alpha)$$

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_{H,N} = - \frac{V(1-T\alpha)}{N C_P} = \frac{V(T\alpha-1)}{C_P}} \quad \mathcal{E}_{J-T}$$

$$\underline{\text{ideal gts}} \quad \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V} \frac{NR}{P} \frac{dT}{dT} = \frac{1}{T}$$

$$\mathcal{E}_{J-T} = 0 !!$$

real gas  $\alpha P < 0$

$T\alpha - 1 < 0 \quad \epsilon_{J-T} < 0 \rightarrow \Delta T > 0$ , gas warms

$T\alpha - 1 > 0 \quad \epsilon_{J-T} > 0 \rightarrow \Delta T < 0$ , gas cools

Basis of vapor compression refrigeration

$\propto$  a function of  $T + P$  for a real gas

vdW fluid as an example

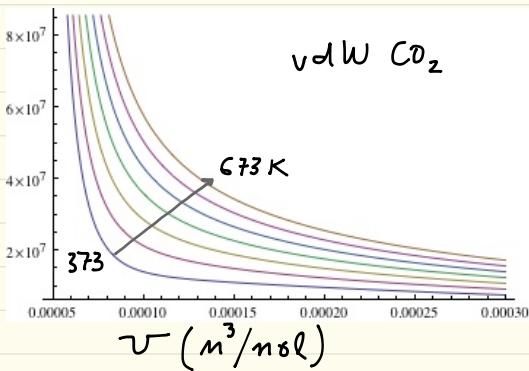
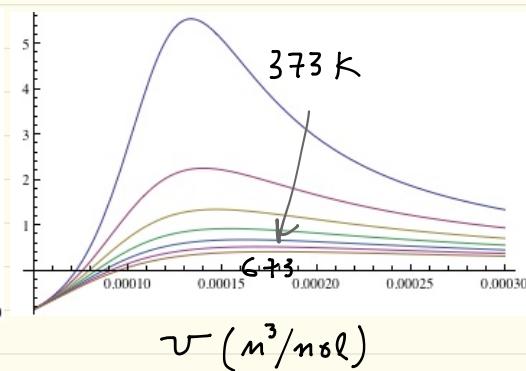
$$P(T, V) = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = -\frac{1}{V} \frac{\left(\frac{\partial P}{\partial T}\right)_V}{\left(\frac{\partial P}{\partial V}\right)_T}$$

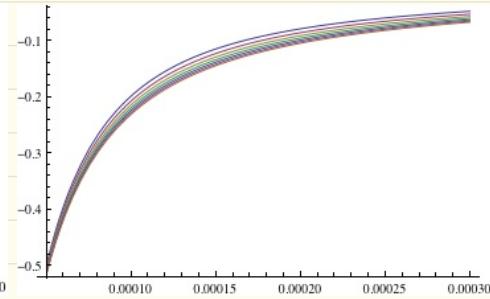
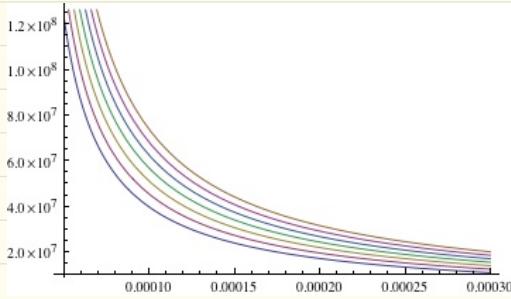
$$\text{Some grinding} \quad \alpha = \frac{R V^2 (V-b)}{R T V^3 - 2a(V-b)^2}$$

$$\frac{1}{\alpha} = \frac{T V}{V-b} - \frac{2a(V-b)}{R V^2}$$

$$CO_2 \quad a = 0.401 \text{ Pa m}^6 \quad b = 42.7 \times 10^{-6} \text{ m}^3$$

$p \text{ (Pa)}$  $v\text{dW } \text{CO}_2$  $673 \text{ K}$  $\rho \text{ (m}^3/\text{mol})$  $T\alpha-1$  $373 \text{ K}$  $\rho \text{ (m}^3/\text{mol})$ 
 $T\alpha-1 > 0 \text{ @ low density / low T}$   
 $< 0 \text{ @ high " / high T}$ 

$$\text{H}_2 \quad a = 0.0248 \text{ Pa} \cdot \text{m}^6 \quad b = 26.6 \times 10^{-6} \text{ m}^3$$



Over similar range of conditions  $\text{H}_2 E_{j-T}$  is uniformly negative — heats up when it expands

Cullen has several other examples (section 7.4) of how similar problems can be solved.

Often we want to know the difference in properties between two states.

How do we get difference between any two arbitrary states?

### thermodynamic tables + charts

Eg Thermo charts

EOS

JANAF tables

NIST webbook

Cahen Table 6.1

} available for limited number of materials

Often provide  $h, s, v$ ; get  $G$  from

$$\underline{g = h - Ts}$$

What if all we know (or can measure or compute) are susceptibilities?

Integrate!

Eg, suppose we want  $s(T, p) - s(T_0, p_0) = \Delta s$

$$ds = \left(\frac{\partial s}{\partial T}\right)_p dT = \frac{C_p}{T} dT \quad \Delta s = \int_{T_0}^T \frac{C_p(T)}{T} dT = \dots$$

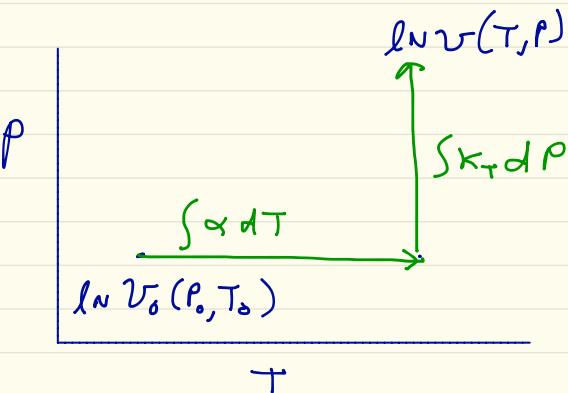
$$v(T, p) - v(T_0, p_0) = \Delta v$$

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

$$= \alpha v dT - v k_T dp$$

$$dv/v = d \ln v = \alpha dT - k_T dp$$

If we know  $\alpha, k_T$  as func of  $T, p$ , integrate along one leg then other

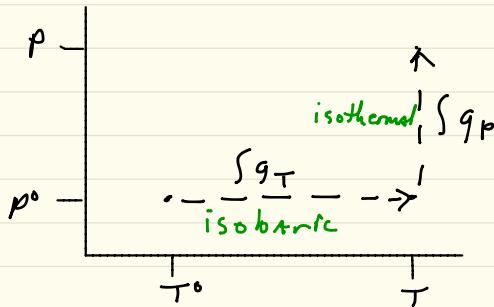


## thermodynamic integration

For a single component system,  $g(T, p) = \mu(T, p)$  is the fundamental eq. Can find  $\mu$  by integrating Gibbs-Duhem:

$$\begin{aligned} d\mu(T, p) &= -SdT + Vdp = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp \\ &= g_T dT + g_p dp \end{aligned}$$

$$\mu = \mu^\circ(T^\circ, p^\circ) + \int_{T^\circ}^T g_T(T, p^\circ) dT + \int_{p^\circ}^p g_p(T, p) dp$$



But what if we don't know  $g_T, g_p$ ?

$$\begin{aligned} -S &= g_T \quad dg_T = g_{TT} dT + g_{Tp} dp = -dS \\ &= -\frac{C_p}{T} dT + \gamma \alpha dP \end{aligned}$$

$$\begin{aligned} V &= g_p \quad dg_p = g_{Tp} dT + g_{pp} dp = dV \\ &= \gamma \alpha dT + \gamma \kappa_T dp \end{aligned}$$

Each of these can be integrated along the isobaric and isothermal paths to give eq

$$-S = g_T = \int_{T_0}^T \left( -\frac{C_p}{T} \right) dT + \int_{P_0}^P v \alpha dP$$

$$V = g_P = \int_{T_0}^T v \alpha dT + \int_{P_0}^P v K_T dP$$

note  $s$  has a constant so that we don't yet know gives a  $(T-T_0) s_0$  term.

Integrating these using the equations above finally give us  $G \equiv \mu$ .

$$\mu(T, P) = \mu_0 - (T-T_0)s_0 + (P-P_0)v_0 - \int_{T_0}^T g_T dT + \int_{P_0}^P g_P dP$$

Thus, from  $\alpha, s_T, C_p$  can recover fundamental eq.

Equivalently, knowing  $C_p$  and the PVT relation gets us the fundamental eq. PVT relation so useful often called THE EOS.

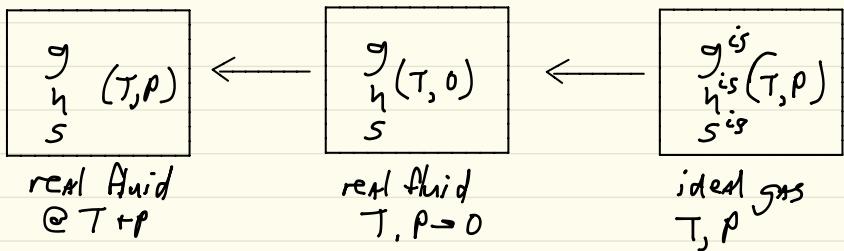
$C_p(T, P)$  in general hard to get at. More commonly have

$$\lim_{P \rightarrow 0} C_p(T, P) = C_p^*(T)$$

ideal gas  $C_p$

$C_p^*(T)$  determined by intramolecular interactions and can be measured, inferred from spectroscopy, or computed !!

Conventional to tabulate thermo data as if fluid was an ideal gas at standard state conditions.



$$\left(\frac{\partial S}{\partial P}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_P = -V\alpha \quad \frac{\text{ideal gas}}{-R/p}$$

$$\left(\frac{\partial h}{\partial P}\right)_T = T \left(\frac{\partial S}{\partial P}\right)_T - V = -V(T\alpha + 1) \quad 0$$

$$\left(\frac{\partial g}{\partial P}\right)_T = -V \quad -\frac{RT}{P}$$

$$S(T, P) = \int_P^0 \left(\frac{\partial V}{\partial T}\right)_P dP + \int_0^P -\frac{R}{P} dP + S^{is}(T, P)$$

$$S(T, P) - S^{is}(T, P) = \int_0^P \left[\left(\frac{\partial V}{\partial T}\right)_P - \frac{R}{P}\right] dP$$

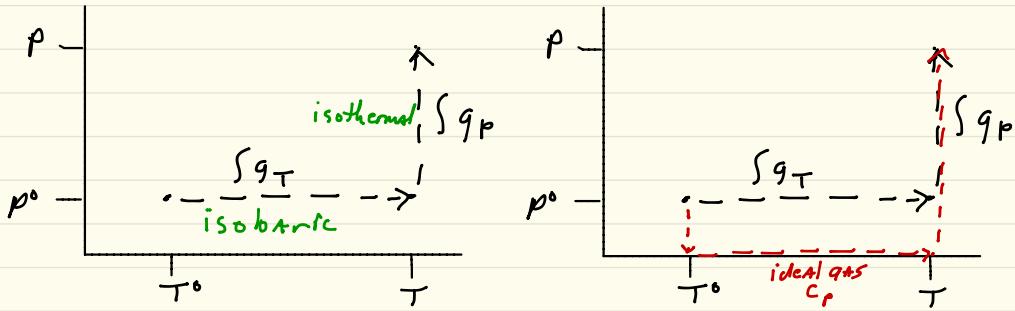
Departure function:  $P = 0$  reference

Residual property - difference between real property and property as if st. was an ideal gas at same  $T + p$ .

Some ambiguity in definitions

Use departure function to compute thermo functions between two states. Becomes departure functions at two points plus ideal gas diff between two points.

Why? Separates mechanical non-ideality ( $P_v T$  relationship) from thermal ( $C_p^{\text{is}}$ ( $T$ )). Tabulate  $C_p^{\text{is}}$ ( $T$ ) ( $h^{\text{is}}$ ,  $s^{\text{is}}$ , ...) and combine w/ EOS.



$$\Delta S_1 = \int_{T_0}^{T_1} \left[ \left( \frac{\partial \bar{v}}{\partial T} \right)_r - \frac{R}{P} \right] dP \Big|_{T=T_0}$$

$$\Delta S_2 = - \int_{T_0}^{T_1} \left[ \left( \frac{\partial \bar{v}}{\partial T} \right)_r - \frac{R}{P} \right] dP \Big|_{T=T_1}$$

} non-ideal corrections

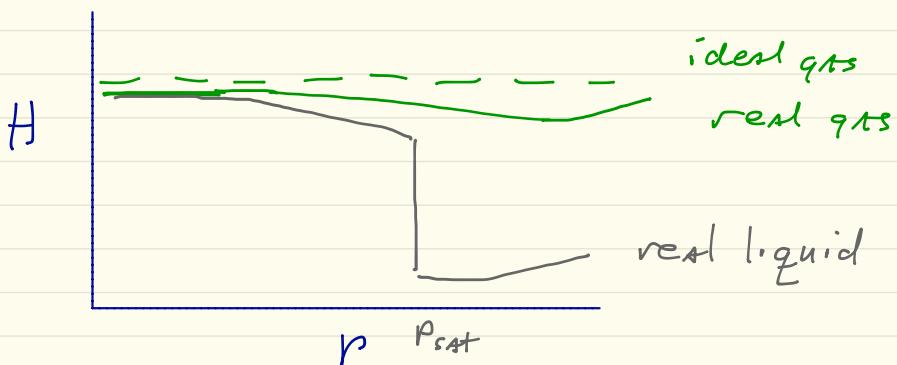
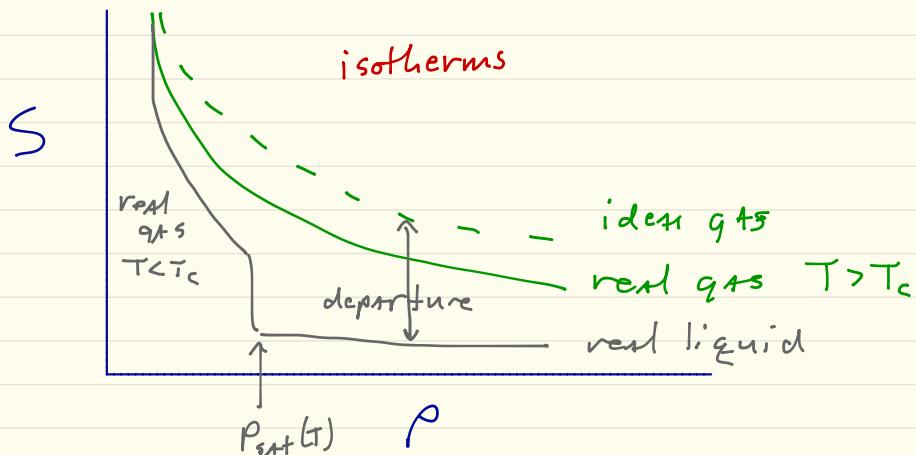
$$\Delta S_2 = \int_{T_0}^{T_1} \frac{C_p^{\text{is}}(T)}{T} dT - R \ln \left( \frac{P}{P_0} \right)$$

} ideal gas  $\Delta S$ !

$$\Delta S_3 = S(T, p) - S^{\text{ideal}}(T, p)$$

called a departure ftn

How much real fluid "departs" @ T, P from what it would be if it was an ideal gas @ T, P



Liquids differ from ideal state much more than gases.

.14

Can always break thermo fns into an ideal gas part and a departure from ideality

$$A_f - A_i = (A_f^{ig} - A_i^{ig}) + (A_f - A_f^{ig}) - (A_i - A_i^{ig})$$

If we are working with  $T$  &  $P$ ,  $T$  and  $v$  are generally more convenient independent variables. Can show

$$S(T, P) - S^{ig}(T, P) = R \ln Z + \int_{\infty}^{v(T, P)} \left[ \left( \frac{\partial P}{\partial T} \right)_v - \frac{R}{v} \right] dv$$

$$H(T, P) - H^{ig}(T, P) = RT(Z-1) + \int_{\infty}^{v(T, P)} \left[ T \left( \frac{\partial P}{\partial T} \right)_v - P \right] dv$$

$$G - G^{ig} = H - H^{ig} - T(S - S^{ig}) \quad \text{departure fns}$$

Can also have  $S(T, v) - S^{ig}(T, v)$   
Hold  $v$  rather than  $P$  const.

Here  $Z = \frac{P(T, v)}{RT} v$  is called the compressibility

Deviation of Pv relationship from ideal gas

Ex H departure ftn for a vdw fluid

$$P = \frac{RT}{v-b} - \frac{a}{v^2}$$

$$Z = \frac{Pv}{RT} = \frac{v}{RT} \left[ \frac{RT}{v-b} - \frac{a}{v^2} \right] = \frac{v}{v-b} - \frac{a}{RTv}$$

$$Z-1 = \frac{v}{v-b} - \frac{a}{RTv}$$

$$RT(Z-1) = \frac{RTb}{v-b} - \frac{a}{v}$$

$$\left( \frac{\partial P}{\partial T} \right)_V = \frac{R}{v-b}$$

$$\int_{\infty}^v \left( T \left( \frac{\partial P}{\partial T} \right)_V - P \right) dv = \int \frac{RT}{v-b} - \left( \frac{RT}{v-b} - \frac{a}{v^2} \right) dv$$

$$= \int \frac{a}{v^2} dv = -\frac{a}{v} \Big|_{\infty}^v = -\frac{a}{v}$$

$$H^{vdw} - H^{ig} = \frac{RTb}{v-b} - \frac{2a}{v}$$

Return (finally) to isenthalpic expansion!

Value of  $q_{AS}$  is isenthalpically expanded from  $T_i, P_i$  to  $P_f$ . What is  $T_f$ ?

$$H(T_f, P_f) = H(T_i, P_i)$$

$$\underbrace{H(T_f, P_f) - H^{\text{ig}}(T_f, P_f)}_{= H(T_i, P_i) - H^{\text{ig}}(T_i, P_i)} = H(T_i, P_i) - H^{\text{ig}}(T_f, P_f)$$

$$= H(T_i, P_i) - H^{\text{ig}}(T_i, P_i)$$

$$+ H^{\text{ig}}(T_i, P_i) - H^{\text{ig}}(T_f, P_f)$$

$$H^{\text{ig}}(T_i, P_i) - H^{\text{ig}}(T_f, P_f) = \int_{T_f}^{T_i} C_p^{\text{ig}}(T) dT$$

$$H(T_i, P_i) - H^{\text{ig}}(T_i, P_i) = \frac{RT_i}{v_i - b} - \frac{2a}{v_i}$$

(have to find  $v_i$  from EOS)

Set equal to  $\frac{RT_f}{v_f - b} - \frac{2a}{v_f}$

Know  $P_f$ , guess  $T_f \rightarrow v_f$ , check if it solves eq.

} sum  
is  
fcn  
of  
 $T_f$