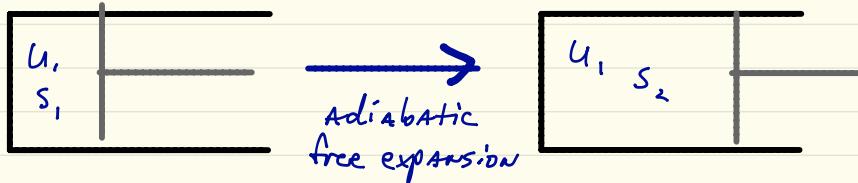
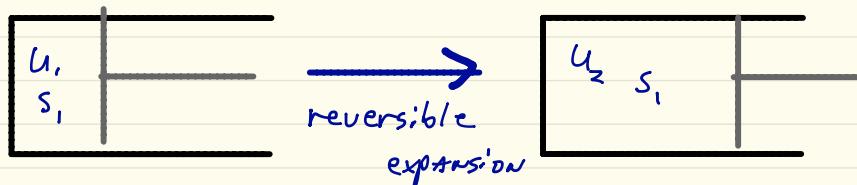


## Lecture 4

### Energy minimum principle



No heat or work,  $\Delta U = 0$ ,  $\Delta S$  maximized



No heat,  $\Delta S = 0$ ,  $\Delta U = dW$  minimized

Intuitively, system expands to minimize  $U$ . Can we prove it?

From our postulates,  $dS = 0$  and  $d^2S \leq 0$  @ equilibrium with respect to any **internal variables**. What about  $dU$  and  $d^2U$ ?

Write:  $dS = \left(\frac{\partial S}{\partial u}\right)_x du + \left(\frac{\partial S}{\partial x}\right)_u dx$   $\times$  an internal DOF

$$dS = 0 \rightarrow \left(\frac{\partial U}{\partial x}\right)_S = -\frac{\left(\frac{\partial S}{\partial x}\right)_u}{\left(\frac{\partial S}{\partial u}\right)_x} = -T_{\text{eq}} \left(\frac{\partial S}{\partial x}\right)_u = 0$$

Shows energy is an extremum @ equilibrium

maximum or minimum?

Let  $(\frac{\partial U}{\partial X})_S = "P"$   $P$  is a function of  $U + X$

$$dP = \left(\frac{\partial P}{\partial U}\right)_X dU + \left(\frac{\partial P}{\partial X}\right)_U dX$$

$$\left(\frac{\partial P}{\partial X}\right)_S = \left(\frac{\partial P}{\partial U}\right)_X \cancel{\left(\frac{\partial U}{\partial X}\right)_S}^0 + \left(\frac{\partial P}{\partial X}\right)_U \cancel{\left(\frac{\partial X}{\partial X}\right)_S}^1$$

$$\left(\frac{\partial P}{\partial X}\right)_S = \left(\frac{\partial P}{\partial X}\right)_U \quad \begin{matrix} \text{derivatives same @ const} \\ S+U \end{matrix}$$

$$\left(\frac{\partial P}{\partial X}\right)_U = \left[ \frac{\partial}{\partial X} \left( \frac{\partial U}{\partial X} \right)_S \right]_U$$

$$= \left[ \frac{\partial}{\partial X} \left\{ -T_{eq} \left( \frac{\partial S}{\partial X} \right)_U \right\} \right]_U \quad \text{from above}$$

$$= -T_{eq} \underbrace{\left( \frac{\partial^2 S}{\partial X^2} \right)_U}_{}.$$

$\leq 0$  @ equilibrium

$$\left(\frac{\partial P}{\partial X}\right)_U = \left(\frac{\partial^2 U}{\partial X^2}\right)_S \geq 0 @ \text{equilibrium}$$

Energy minimum principle - when a constraint is relaxed at constant  $S$ , the system relaxes to the state of minimum energy

From this the same conditions on equilibrium can be found,  $T_1 = T_2, \dots$

(3)

This by itself isn't so useful, but it leads to useful stuff.

A basic problem is that the extensive variables, especially  $S$ , aren't so convenient as independent variables.  $T, P$  — those are nice to measure & control.

**Legendre transform** provides way to do this change of variables

Given a function  $Y = Y(x)$  fundamental eq  
 $P = \frac{dY}{dx}$  intensive variable

Legendre transform  $\Psi(P) = Y - PX$

contains all the same information as the original function. Legendre transform on  $\Psi$  recovers  $Y$ .

Can apply to multi-dimensional functions in same way.

(As an aside, Hamiltonian mechanics, which use positions & momenta as variables, is a Legendre transform on the Lagrangian mechanics of positions & velocities.)

$$\text{Example } Y = \frac{1}{4}x^2$$

$$y = mx + b$$

$$b = y - mx$$

$$y - \left(\frac{dy}{dx}\right)x$$

$$p = \frac{dy}{dx} = \frac{1}{2}x$$

$$\psi(p) = Y - pX = p^2 - p(2p) = -p^2$$

P, slope

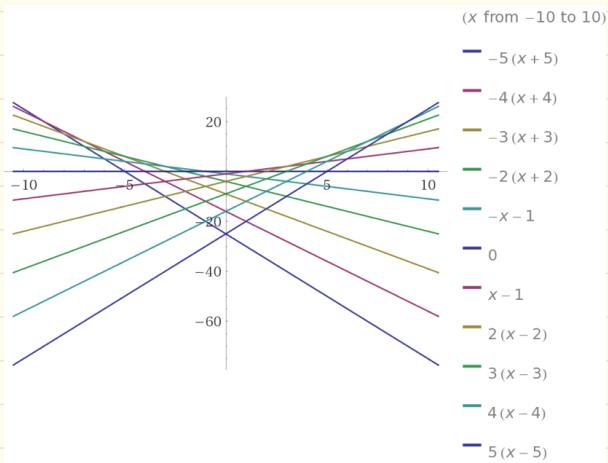
-2  
-1  
0  
1  
2

$\psi(p)$ , intercept

-4  
-2  
0  
-2  
-4

family of lines  
whose tangents  
define  $Y$

$$Y = \frac{1}{4}x^2$$



plot

$p x - p^2$  where  $p = \{-5, -4, -3, -2, -1, 0, 1, 2, 3, 4, 5\}$

4

Enthalpy  $H \equiv H(S, V, N)$  Legendre transform  $V$

$$H = U - \left(\frac{\partial U}{\partial V}\right)_{S, N} V$$

$$H = U + PV$$

$$dH = dU + d(PV)$$

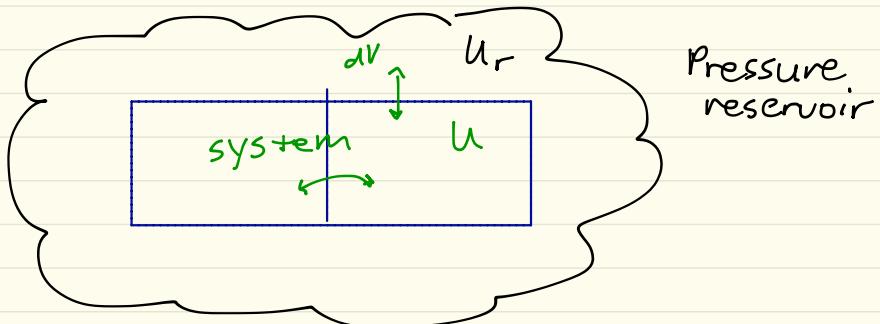
$$= TdS - PdV + \sum_i \mu_i dN_i + PdV + VdP$$

$$dH = TdS + VdP + \sum_i \mu_i dN_i$$

Enthalpy is a state function and is a natural function of  $S, P, N$

$$H = H(S, P, N_i)$$

$$\left(\frac{\partial H}{\partial S}\right)_{P, N_i} = T \quad \left(\frac{\partial H}{\partial P}\right)_{S, N_i} = V \quad \left(\frac{\partial H}{\partial N_j}\right)_{S, P, V, i \neq j} = \mu_j$$



Assume the reservoir much much bigger than the system, so  $P_r$  invariant to small changes in volume

(5)

Relax some constraint on system so it goes to a new equilibrium.

$$dU_{\text{tot}} = dU + dU_r = 0 \quad @ \text{constant } S$$

System + reservoir only exchange volume, so

$$\begin{aligned} dU_r &= -P_r dV_r \\ dV_r &= -dV \quad dU_{\text{tot}} = dU + P_r dV \\ &= d(U + P_r dV) \quad (\text{const } P_r = P) \\ &= dH \end{aligned}$$

$dH = 0$  @ equilibrium at constant pressure.

Further,  $d^2H = d^2(U + PV)$

$$\begin{aligned} &= d^2U + P \underset{\substack{\rightarrow 0 \\ \text{tot}}}{d^2V} \quad U \text{ an independent variable, so its} \\ &\quad \text{2nd derivative with other internal variables vanishes} \\ d^2H &= d^2U \underset{\substack{\rightarrow 0 \\ \text{tot}}}{} > 0 \end{aligned}$$

Like  $U$ ,  $H$  is minimized @ equilibrium over the set of states with  $P = P_r$ .

$$H = U + PV$$

$H$  is the internal energy of a system, including the energy to make "space" for it in the environment

Recall Euler equation  $U = TS - PV + \sum \mu N$

Combining,  $H = TS - \sum \mu N$

From definition of heat capacity,

$$C_p = \frac{1}{N} \left( \frac{\partial S}{\partial T} \right)_{p,N} = \frac{1}{N} \left( \frac{\partial H}{\partial T} \right)_{n,p} = \frac{1}{N} \left( \frac{\partial q_{as}}{\partial T} \right)_p$$

$$dH = \partial q_{as}$$

Enthalpy is thus heat flow at constant pressure and when system experiences only PV work. Common situation, which makes enthalpy useful.

Enthalpy of an ideal gas?

$$U = cNRT \quad H = U + PV = cNRT + NRT = (c+1)NRT$$

enthalpy of an ideal gas is a natural, exclusive function of T (as is its derivatives).

Could, with difficulty, convert into  $H(S, P, N)$ , using S expression of ideal gas.

$$C_{p,ig} = \left( \frac{\partial H_{ig}}{\partial T} \right)_{n,p} = (c+1)R = C_{v,ig} + R$$

State functions have the property that cross-derivatives are equal:

$$df = \underbrace{\left(\frac{\partial f}{\partial x}\right)_y dx}_{A(x,y)} + \underbrace{\left(\frac{\partial f}{\partial y}\right)_x dy}_{B(x,y)}$$

$$\left(\frac{\partial A}{\partial y}\right)_x = \left(\frac{\partial B}{\partial x}\right)_y$$

because order of differentiation doesn't matter

Basis of so-called "Maxwell relations"

$$dH = TdS + VdP + \sum_i \mu_i dN_i$$

$$\left(\frac{\partial T}{\partial P}\right)_{S,N} = \left(\frac{\partial V}{\partial S}\right)_{P,N}$$

$$\left(\frac{\partial T}{\partial N}\right)_{S,P} = \left(\frac{\partial \mu}{\partial S}\right)_{P,N}$$

$$\left(\frac{\partial V}{\partial N}\right)_{S,P} = \left(\frac{\partial \mu}{\partial P}\right)_{S,N}$$

We'll use these when we apply enthalpy

## Helmholtz potential

$U \equiv U(S, V, N)$  Legendre transform S

$$F = U - \left(\frac{\partial U}{\partial S}\right)_{V, N} S$$

$$F = U - TS$$

$$dF = dU - d(TS)$$

$$= TdS - PdV + \mu dN - TdS - SdT$$

$$dF = -SdT - PdV + \mu dN$$

F is a natural function of  $T, V, N$ ,  $F(T, V, N)$

$$\left(\frac{\partial F}{\partial T}\right)_{V, N} = -S \quad \left(\frac{\partial F}{\partial V}\right)_{T, N} = -P \quad \left(\frac{\partial F}{\partial N}\right)_{T, V} = \mu$$

Euler relation gives

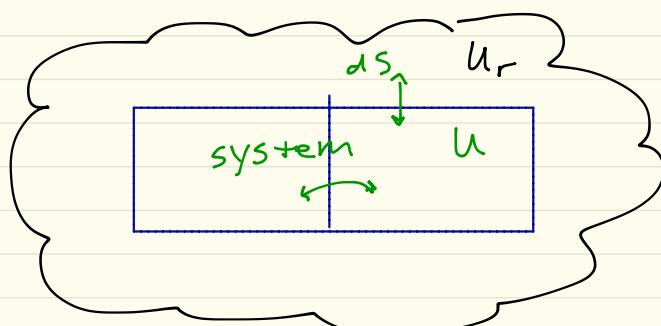
$$F = -PV + \sum \mu N$$

$$\left(\frac{\partial S}{\partial V}\right)_{N, T} = \left(\frac{\partial P}{\partial T}\right)_{N, V}$$

Maxwell relations

$$\left(\frac{\partial S}{\partial N}\right)_{T, V} = \left(\frac{\partial \mu}{\partial T}\right)_{N, V}$$

$$\left(\frac{\partial P}{\partial N}\right)_{T, V} = \left(\frac{\partial \mu}{\partial V}\right)_{N, T}$$



Temperature reservoir

Assume the reservoir much much bigger than the system, so  $T_r$  invariant to small changes in entropy.

Relax some constraint on system so it goes to a new equilibrium.

$$dU_{\text{tot}} = dU + dU_r = 0 \quad @ \text{constant } S$$

System + reservoir only exchange heat, so

$$dU_r = T_r dS_r$$

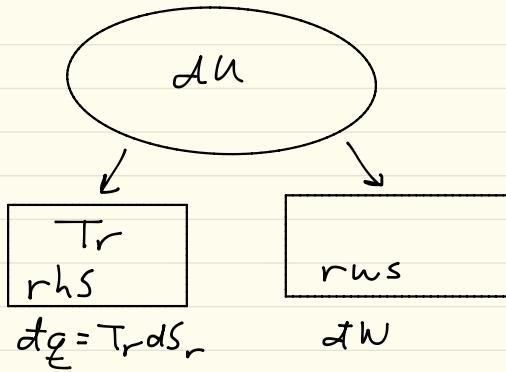
$$\begin{aligned} dS_r &= -dS \quad dU_{\text{tot}} = dU + T_r dS_r \\ &= d(U - T_r dS) \quad (\text{const } T_r = T) \\ &= dF \end{aligned}$$

$dF = 0$  @ equilibrium at constant temperature

Also,  $\partial^2 F > 0$  @ equilibrium

Helmholtz potential minimized @ equilibrium over manifold of states with  $T = T_r$ .

reversible  
work  
theorem



$$dU + dq + dw = 0 \quad dS + dS_r = 0$$

$$dU - Tr dS = - dw \rightarrow \boxed{dF = - dw}$$

$F$  is thus the "free energy," the maximum amount of work extractable in contact with a thermal reservoir.

Helmholtz free energy of an ideal gas?

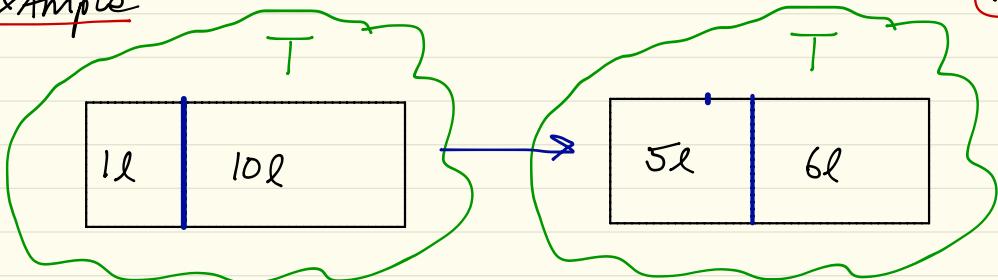
$$F = U - TS = cNRT - TS(T, V, N)$$

$$S(T, V, N) = cNR \ln \frac{T}{T_0} + NR \ln \frac{V}{V_0} \frac{N_0}{N} + Ns_0$$

$$\begin{aligned} F &= cNRT - TNs_0 + NRT \ln \left\{ \left( \frac{T}{T_0} \right)^c \left( \frac{V}{V_0} \right) \left( \frac{N_0}{N} \right) \right\} \\ &= \left( \frac{NT}{N_0 T_0} \right) \left( cN_0 RT_0 - N_0 T_0 s_0 \right) + NRT \ln \dots \end{aligned}$$

$$\boxed{F_{ig} = NRT \left\{ \frac{F_0}{N_0 RT_0} + \ln \left\{ \left( \frac{T}{T_0} \right)^c \left( \frac{V}{V_0} \right) \left( \frac{N_0}{N} \right) \right\} \right\}}$$

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example

1 mole in each chamber, ideal gases

$$@ \text{constant } T, N, \quad F = \text{const} - NRT \ln \left( \frac{V}{V_0} \right)$$

$$\Delta F = -NRT \left\{ \ln 5 + \ln 6 - \ln 1 - \ln 10 \right\} = -NRT \ln 3 \\ @ 273K = -2.5 \text{ kJ}$$

Free energy  $\downarrow \rightarrow W_{\text{done}}$

## Gibbs potential

$$U \equiv U(S, V, N)$$

Legendre transform S and V

$$G = U - \left(\frac{\partial U}{\partial S}\right)_{V, N} S - \left(\frac{\partial U}{\partial V}\right)_{S, N} V$$

$$G = U - TS + PV$$

$$dG = dU - d(TS) + d(PV)$$

$$= TdS - PdV - TdS - SdT + PdV + VdP + \sum_i \mu_i dN_i$$

$$dG = -SdT + VdP + \sum_i \mu_i dN_i$$

G is a natural function of T, P, N

$$\left(\frac{\partial G}{\partial T}\right)_{P, N} = -S \quad \left(\frac{\partial G}{\partial P}\right)_{T, N} = V \quad \left(\frac{\partial G}{\partial \mu_i}\right)_{T, P} = \mu_i$$

Euler relation gives

$$G = \sum_i \mu_i N_i$$

For a single component system, the molar Gibbs energy is  $\mu$ .

$$G/N = \mu \quad \frac{G}{N} = \sum_i \mu_i dX_i$$

For this reason  $\mu$  is often called molar Gibbs energy and  $\mu_i$  partial molar Gibbs energy.

Gibbs energy is minimized at equilibrium for a system in communication with a constant T and P reservoir. Corresponds to maximum work that can be extracted at constant T + P.

Most widely applied to problems in chemical equilibria. We will return to this.

### Maxwell relations

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

$$-\left(\frac{\partial S}{\partial N_i}\right)_{T,P} = \left(\frac{\partial \mu_i}{\partial T}\right)_{P,N}$$

$$\left(\frac{\partial V}{\partial N_j}\right)_{P,T} = \left(\frac{\partial \mu_i}{\partial P}\right)_{N,T}$$

everything potential ( $A$  for all es)

$U = U(S, V, N)$  Legendre transform  $S, V, N$

$$A = U - \left(\frac{\partial U}{\partial S}\right)S - \left(\frac{\partial U}{\partial V}\right)V - \left(\frac{\partial U}{\partial N}\right)_N$$

$$= U - TS + PV - \mu N \quad \downarrow \quad \text{Given Euler form of } U$$

$$= 0 !!$$

$A$  is a natural function of  $T, P, \mu$

$$dA = -SdT + VdP - Nd\mu = 0$$

Gibbs-Duhem relation recovered !!

See, it all hangs together...

## Susceptibilities

First derivatives of  $S, U \rightarrow$  intensive thermo properties

Second " " " "  $\rightarrow$  material properties

### coefficient of thermal expansion

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_{P,V}$$

fractional increase in volume  
with  $T$  ( $\equiv dV/dS$ )

ideal gas  $\alpha = \frac{1}{T} > 0$

### isothermal compressibility

$$\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

fractional decrease in volume  
with  $P$  ( $\equiv dV/dU$ )

ideal gas  $\kappa_T = 1/P > 0$

### constant pressure heat capacity

$$C_p = \frac{T}{N} \left( \frac{\partial S}{\partial T} \right)_P = \frac{1}{N} \left( \frac{\partial q_{rev}}{\partial T} \right)_P$$

$$\begin{aligned} \text{ideal gas } S(T, P, N) &= cNR \ln\left(\frac{T}{T_0}\right) + NR \ln\left[\frac{RT}{P} \cdot \frac{P_0}{RT_0}\right] + \text{const} \\ &= (c+1)NR \ln\left(\frac{T}{T_0}\right) + NR \ln\left(\frac{P_0}{P}\right) + \text{const} \end{aligned}$$

$$\frac{T}{N} \left( \frac{\partial S}{\partial T} \right)_P = \frac{T}{N} (c+1)NR \cdot \frac{1}{T} = \underline{(c+1)R} > 0$$

Constant volume heat capacity

$$C_v = \frac{1}{N} \left( \frac{dS}{dT} \right)_v = \frac{1}{N} \left( \frac{dq}{dT} \right)_v \text{ ideal gts } C_v = cR$$

All other susceptibilities can be related to these 3

### Example

vdW coefficient of isothermal compressibility

$$\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \rightarrow \left( \frac{\partial P}{\partial V} \right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3}$$

$$\rightarrow V \left( \frac{\partial P}{\partial V} \right)_T = \frac{2a}{V^2} - \frac{RTV}{(V-b)^2}$$

$$\kappa_T = \frac{1}{\frac{RTV}{(V-b)^2} - \frac{2a}{V^2}} = \frac{V^2(V-b)^2}{RTV^3 - 2a(V-b)^2}$$

Fun, fun... is this always  $> 0$ ? NO!

Reflects regions of instability. We'll return to this.

The second derivatives of  $G$  have special significance at constant  $N$ :

$$\left(\frac{\partial^2 g}{\partial T^2}\right)_{P,N} = - \left(\frac{\partial s}{\partial T}\right)_{P,N} = - \frac{C_p}{T} \quad \text{heat capacity!}$$

$$\left(\frac{\partial^2 g}{\partial P^2}\right)_{T,N} = \left(\frac{\partial v}{\partial P}\right)_{T,N} = -v \kappa_T \quad \text{isothermal compressibility!}$$

$$\left(\frac{\partial^2 g}{\partial T \partial P}\right)_N = \left(\frac{\partial v}{\partial T}\right)_{P,N} = v \alpha \quad \text{coefficient of thermal expansion!}$$

These 3 form a "complete set". All 1st derivatives @ constant  $N$  can be expressed in terms of these.

## Joule-Thomson effect as an example

$$\begin{array}{c} P_i \quad | \quad v_i \quad \xrightarrow{\text{plug}} \quad v_f > v_i \quad | \quad P_f < P_i \\ \hline T_i \quad \text{plug or } T_f \neq T_i \\ \text{restriction} \end{array}$$

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 semi-adiabatic 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.

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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

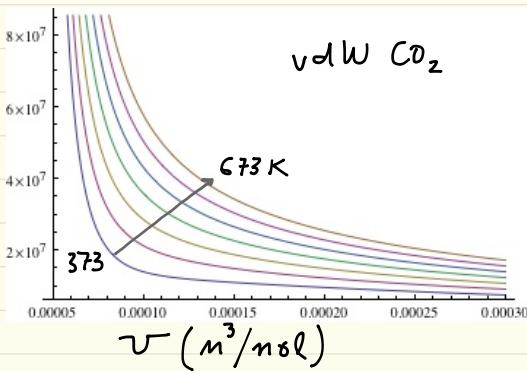
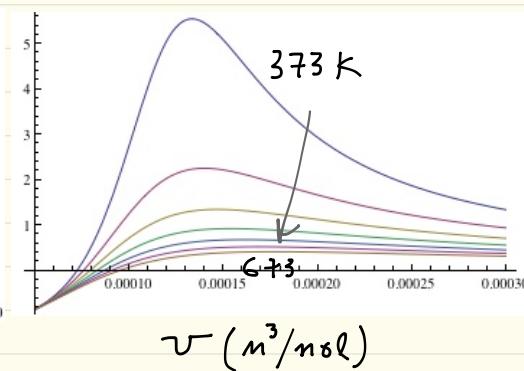
$$P(T, V) = \frac{RT}{V-b} - \frac{a}{V^2}$$

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

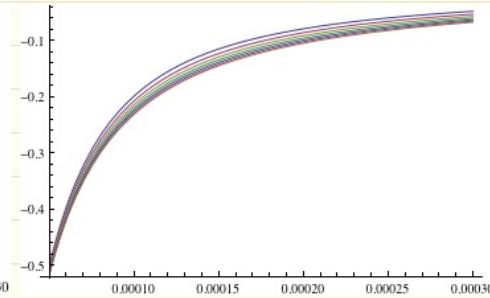
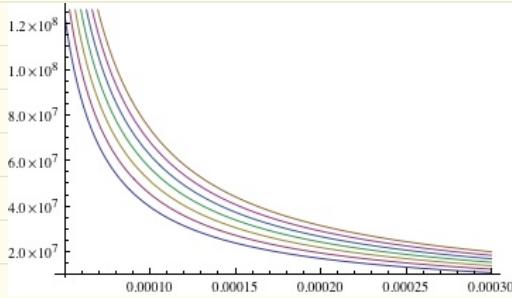
$$\text{Some grinding} \quad \alpha = \frac{R V^2 (V-b)}{R T V^3 - 2a(V-b)^2}$$

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

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

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

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



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. Fundamental equation for single component system is

$$G(T, P, N) = N\mu$$

How do we get difference between any two arbitrary states?

### thermodynamic tables + charts

Eg Thermo charts

EOS

JANAF tables

NIST webbook

Cochran Table 6.1

} available for limited number of materials

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

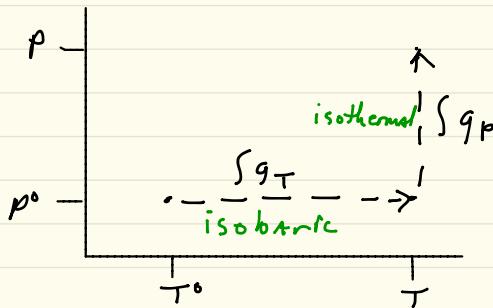
$$\underline{g = h - Ts}$$

## thermodynamic integration

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

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

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



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

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

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

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

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

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

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

$$\mu(T, P) = \mu_0 - (T - T_0) S_0 + (P - P_0) v_0 - \int_{T_0}^T g_T dT + \int_{P_0}^P g_P dP$$

Thus, from  $\alpha, \kappa_T, C_p$  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 gts  $C_p$

$C_p^*(T)$  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.

$$\begin{matrix} g \\ h \\ s \end{matrix} (T, p)$$

real fluid  
@  $T + p$

$$\begin{matrix} g \\ h \\ s \end{matrix} (T, 0)$$

real fluid  
 $T, p \rightarrow 0$

$$\begin{matrix} g^{is} \\ h^{is} \\ s^{is} \end{matrix} (T, p)$$

ideal gas  
 $T, p$

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

ideal gas  
 $- R/p$

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

$$\left( \frac{\partial g}{\partial P} \right)_T = - \nu$$

$- \frac{RT}{P}$

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

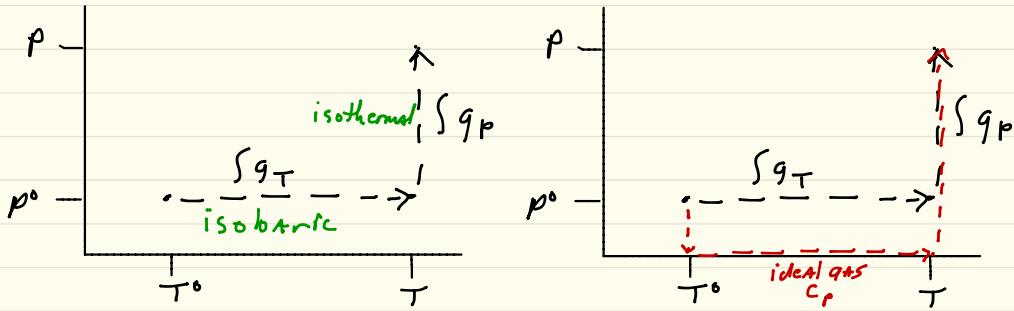
$$S(T, P) - S^{is}(T, P) = \int_0^P \left[ \left( \frac{\partial V}{\partial T} \right)_P - \frac{R}{P} \right] dP$$

## Departure Function

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

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.



$$\Delta S_1 = \int_{T_0}^{P_0} \left[ \left( \frac{\partial \bar{v}}{\partial T} \right)_r - \frac{R}{P} \right] dP \Big|_{T=T_0}$$

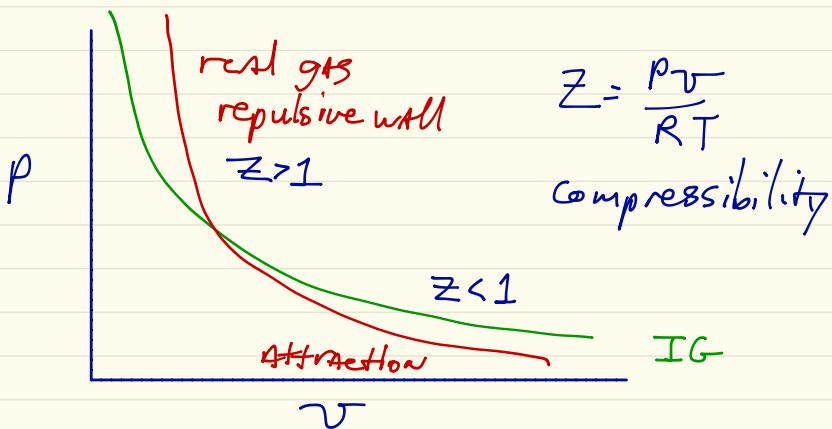
$$\Delta S_2 = - \int_{T_0}^P \left[ \left( \frac{\partial \bar{v}}{\partial T} \right)_r - \frac{R}{P} \right] dP \Big|_{T=T}$$

} non-ideal corrections

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

ideal gas  $\Delta S$ !

For fluids PVT can be measured. Encodes information about intermolecular interactions



Fluids are non-ideal because

- molecules have volume, repel at short distances

$$P > P_{ig} \quad Z > 1$$

- molecules attract one another

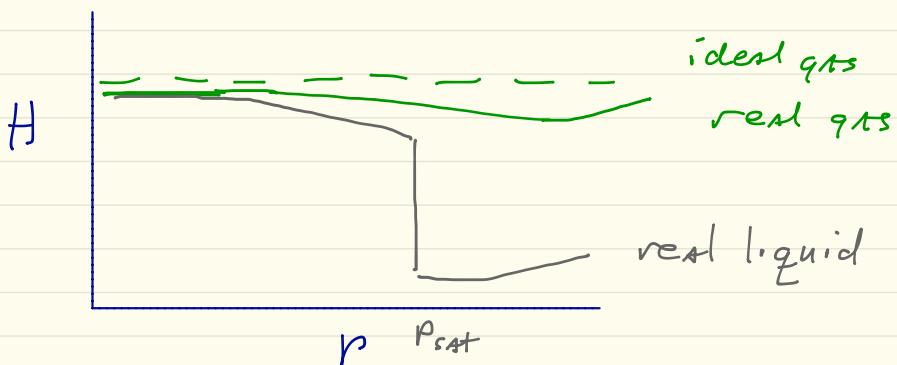
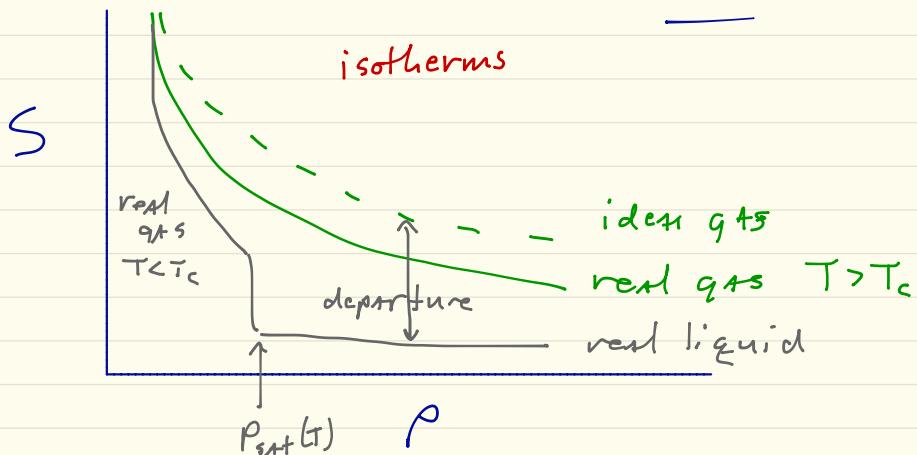
$$P < P_{ig} \quad Z < 1$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial ZRT/P}{\partial T}\right)_P = \frac{R}{P} \left[ Z + T \left( \frac{\partial Z}{\partial T} \right)_P \right]$$

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

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.

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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.

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!

Volume gas is isenthalpically expanded from  $T_i, P_i$  to  $P_f$ . What is  $T_f$ ?

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

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

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

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

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

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

(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.

Why do we care about these susceptibilities?  
 Can be tabulated (or calculated from first principles!) to compute extensive variables at different conditions.

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

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

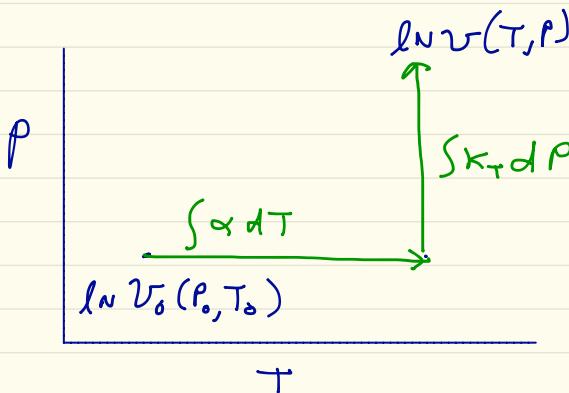
$$v(T, p) - v(T_0, p_0) = \Delta v$$

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

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

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

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



Can derive important relationship between  $G$  and  $H$ :

$$G = H - TS \rightarrow \frac{G}{T} = \frac{H}{T} - S$$

$$\begin{aligned}\left(\frac{\partial(G/T)}{\partial T}\right)_{P,V} &= \frac{\partial(H/T)}{\partial T} - \left(\frac{\partial S}{\partial T}\right) \\ &= -\frac{H}{T^2} + \underbrace{\frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_P}_{= 0!}\end{aligned}$$

$$\left(\frac{\partial(G/T)}{\partial T}\right)_{P,V} = -\frac{H}{T^2}$$

Similarly,

$$\left(\frac{\partial(F/T)}{\partial T}\right)_{P,V} = -\frac{U}{T^2}$$

Gibbs-Helmholtz relation  
T-dependence of  $G$   
related to  $H$ !

Very commonly used  
relation in chemical  
systems.