

## Chem 340 - Lecture Notes 4 – Fall 2013 – State function manipulations

### Properties of State Functions

State variables are **interrelated** by equation of state, so they are **not independent**, express relationship mathematically as a partial derivative, and **only need two of T, V, P**

**Example:** Consider ideal gas:  $PV = nRT$  so  $P = f(V, T) = nRT/V$ , let  $n=1$

Can now do derivatives:  $(\partial P/\partial V)_T = -RT/V^2$  and :  $(\partial P/\partial T)_P = R/V$

Full differential show variation with respect to one variable at a time, sum for both:

(equations all taken from Engel, © Pearson)

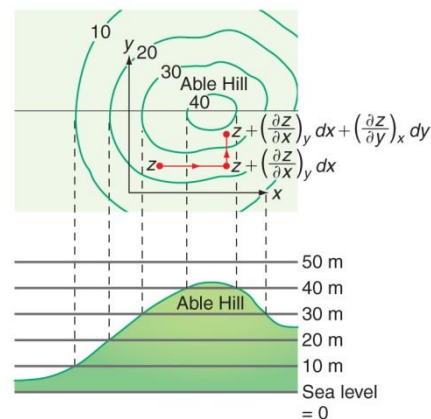
$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV$$

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shows total change in P if have some change in V and in T

**Example,** on hill and want to know how far down (dz) you will go if move some amount in x and another in y. contour map can tell, or if knew function could compute  $dz_x$  from  $dz/dx$  for motion in x and  $dz_y$  from  $dz/dy$  for motion in y total change in z is just sum:  $dz = (dz/dx)_y dx + (dz/dy)_x dy$

Note: for dz, small change (big ones need higher derivative)



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Can of course keep going with 2<sup>nd</sup> and 3<sup>rd</sup> derivatives or mixed ones

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial P}{\partial V}\right)_T\right)_V = \frac{\partial^2 P}{\partial T \partial V} = \left(\frac{\partial}{\partial T}\left(\frac{\partial}{\partial V}\left[\frac{RT}{V}\right]\right)_T\right)_V = \left(\frac{\partial}{\partial T}\left[-\frac{RT}{V^2}\right]\right)_V = -\frac{R}{V^2}$$

$$\left(\frac{\partial}{\partial V}\left(\frac{\partial P}{\partial T}\right)_V\right)_T = \frac{\partial^2 P}{\partial V \partial T} = \left(\frac{\partial}{\partial V}\left(\frac{\partial}{\partial T}\left[\frac{RT}{V}\right]\right)_V\right)_T = \left(\frac{\partial}{\partial V}\left[\frac{R}{V}\right]\right)_T = -\frac{R}{V^2}$$

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For state functions the **order of taking the derivative** is not important, or

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial f(V, T)}{\partial V}\right)_T\right)_V = \left(\frac{\partial}{\partial V}\left(\frac{\partial f(V, T)}{\partial T}\right)_V\right)_T$$

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The corollary works, **reversed derivative equal** → determine if property is state function

as above, **state function** has an **exact differential**:  $\Delta f = \int df = f_f - f_i$

good examples are  $\Delta U$  and  $\Delta H$ , but, **q** and **w** are not state functions

**Some handy calculus things:**

If  $z = f(x,y)$  can rearrange to  $x = g(y,z)$  or  $y = h(x,z)$  [e.g.  $P=nRT/V$ ,  $V=nRT/P$ ,  $T=Pv/nR$ ]

Inversion:  $\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}$  cyclic rule:  $\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$

So we can evaluate  $(\partial P/\partial V)_T$  or  $(\partial P/\partial T)_V$  for **real system**, use cyclic rule and inverse:

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

divide both sides by  $(\partial T/\partial P)_V$  get  $1/(\partial T/\partial P)_V = (\partial P/\partial T)_V$

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = -\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} = \frac{\beta}{\kappa} \quad \text{and}$$

similarly  $(\partial P/\partial V)_T = 1/(\partial V/\partial P)_T$  so get **ratio of two volume changes**

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

cancel  $(\partial V/\partial T)_P = \beta V$  const.  $\beta, \kappa$  norm to  $V$

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$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \quad \text{and} \quad \kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$$

Where:  $\beta$  = volumetric thermal expansion coefficient (**Atkins**  $\rightarrow \alpha$ ) and  $\kappa$  = isothermal compressibility

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**Point:** We can **measure both** of these properties and solve relationships, **for any system**  
 Sign chosen so  $\kappa$  is **positive** (i.e. as  $P$  inc., expect  $V$  dec.,  $(\partial V/\partial P)_T$  negative)

Back to start, **total derivative, dP:** integrate:

$$dP = \frac{\beta}{\kappa} dT - \frac{1}{\kappa V} dV \quad \Delta P = \int_{T_i}^{T_f} \frac{\beta}{\kappa} dT - \int_{V_i}^{V_f} \frac{1}{\kappa V} dV \approx \frac{\beta}{\kappa} (T_f - T_i) - \frac{1}{\kappa} \ln \frac{V_f}{V_i}$$

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**Example:** temperature in experiment has risen so ethanol thermometer is at the top of capillary, filled. If you increase another 10°C, how much will pressure increase?

$$\Delta P = \int (\beta_{et}/\kappa) dT - \int (1/\kappa V) dV \sim \beta_{et} \Delta T / \kappa - (1/\kappa) \ln(V_f/V_i) \quad V_f = V_i(1 + \beta_{gl} \Delta T) \quad \ln(1-x) \sim -x, x \ll 1$$

$$\Delta P = \beta_{et} \Delta T / \kappa - (\beta_{gl} \Delta T / \kappa) \quad \ln(V_f/V_i) = \ln(1 + \beta_{gl} \Delta T) \sim \beta_{gl} \Delta T$$

$$\Delta P = (\Delta T / \kappa) (\beta_{et} - \beta_{gl}) \quad \beta_{gl} = 2.0 \times 10^{-5} \text{ } ^\circ\text{C}^{-1} \quad \beta_{et} = 11.2 \times 10^{-4} \text{ } ^\circ\text{C}^{-1} \quad \kappa = 11.0 \times 10^{-5} \text{ bar}^{-1}$$

$$\Delta P = (10 \text{ } ^\circ\text{C} / 11.0 \times 10^{-5} \text{ bar}^{-1}) (11.2 - 0.2) \times 10^{-4} \text{ } ^\circ\text{C}^{-1} = 100 \text{ bar} \quad (\text{goodbye thermometer!})$$

$\kappa$  and  $\beta$  ( $\alpha$ -Atkins) values for selected solids and liquids:

TABLE 3.1 Volumetric Thermal Expansion Coefficient for Solids and Liquids at 298 K			
Element	$10^6 \beta / (\text{K}^{-1})$	Element or Compound	$10^4 \beta / (\text{K}^{-1})$
Ag(s)	57.6	Hg(l)	1.81
Al(s)	69.3	CCl <sub>4</sub> (l)	11.4
Au(s)	42.6	CH <sub>3</sub> COCH <sub>3</sub> (l)	14.6
Cu(s)	49.5	CH <sub>3</sub> OH(l)	14.9
Fe(s)	36.9	C <sub>2</sub> H <sub>5</sub> OH(l)	11.2
Mg(s)	78.3	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> (l)	10.5
Si(s)	7.5	C <sub>6</sub> H <sub>6</sub> (l)	11.4
W(s)	13.8	H <sub>2</sub> O(l)	2.04
Zn(s)	90.6	H <sub>2</sub> O(s)	1.66

Sources: Benenson, W., Harris, J. W., Stocker, H., and Lutz, H. *Handbook of Physics*. New York: Springer, 2002; Lide, D. R., ed. *Handbook of Chemistry and Physics*. 83rd ed. Boca Raton, FL: CRC Press, 2002; Blachnik, R., ed. *D'Ans Lax Taschenbuch für Chemiker und Physiker*. 4th ed. Berlin: Springer, 1998.

Liquid  $\beta$  ( $\alpha$ ) values generally much larger than for solids, see example above

Note: water will be different close to 273 K, max density ~4 C

TABLE 3.2 Isothermal Compressibility at 298 K			
Substance	$10^6 \kappa / \text{bar}^{-1}$	Substance	$10^6 \kappa / \text{bar}^{-1}$
Al(s)	1.33	Br <sub>2</sub> (l)	64
SiO <sub>2</sub> (s)	2.57	C <sub>2</sub> H <sub>5</sub> OH(l)	110
Ni(s)	0.513	C <sub>6</sub> H <sub>5</sub> OH(l)	61
TiO <sub>2</sub> (s)	0.56	C <sub>6</sub> H <sub>6</sub> (l)	94
Na(s)	13.4	CCl <sub>4</sub> (l)	103
Cu(s)	0.702	CH <sub>3</sub> COCH <sub>3</sub> (l)	125
C(graphite)	0.156	CH <sub>3</sub> OH(l)	120
Mn(s)	0.716	CS <sub>2</sub> (l)	92.7
Co(s)	0.525	H <sub>2</sub> O(l)	45.9
Au(s)	0.563	Hg(l)	3.91
Pb(s)	2.37	SiCl <sub>4</sub> (l)	165
Fe(s)	0.56	TiCl <sub>4</sub> (l)	89
Ge(s)	1.38		

Sources: Benenson, W., Harris, J. W., Stocker, H., and Lutz, H. *Handbook of Physics*. New York: Springer, 2002; Lide, D. R., ed. *Handbook of Chemistry and Physics*. 83rd ed. Boca Raton FL: CRC Press, 2002; Blachnik, R., ed. *D'Ans Lax Taschenbuch für Chemiker und Physiker*. 4th ed. Berlin: Springer, 1998.

Now look at how **U** varies with **V** and **T**, since state function can do same things

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad \text{but } \Delta U = q + w \text{ and differential: } dU = \delta q + \delta w$$

$$\text{So } dU = \delta q - P_{\text{external}} dV = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

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$$\text{If } dV = 0, \quad \delta q_V = \left(\frac{\partial U}{\partial T}\right)_V dT \quad \text{so} \quad \frac{\delta q_V}{dT} = \left(\frac{\partial U}{\partial T}\right)_V = C_V \quad \text{like state fct, if } V \text{ const} \rightarrow \text{path}$$

Already discuss  $C_V$ : positive, extensive,  $C_{V,m} = C_V/n$  intensive, vary with substance and  $T$

**Microscopic picture:** due to the variation in accessible energy states, so more degrees of freedom (rotations, vibrations) for polyatomics as opposed to atoms

$$\left| \begin{array}{l} \Delta U_V = \int_{T_1}^{T_2} C_V dT = n \int_{T_1}^{T_2} C_{V,m} dT \quad \text{or} \quad \int_i^f \delta q_V = \int_i^f \left(\frac{\partial U}{\partial T}\right)_V dT \quad \text{or} \quad q_V = \Delta U \end{array} \right.$$

$\delta q$  is inexact but if path defined has unique value, here constant  $V$ , so  $q_V$  eval,  $C_V$  fixed

that was one part of complete differential, what about:  $(\partial U / \partial V)_T = \pi_T$  - internal pressure

$$\text{Can show that } \left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P \quad \text{put it into} \quad dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$dU = dU_V + dU_T = C_V dT + \left[ T \left(\frac{\partial P}{\partial T}\right)_V - P \right] dV \quad \begin{array}{l} \text{Ideal gas, } \pi_T = 0, \text{ no interaction} \\ \text{work out: } T[\partial(nRT/V)/\partial T]_V - P = \\ T(nR/V) - P = P - P = 0 \end{array}$$

so ideal gas  $dU = C_V dT$  (but do not need const  $V$ !)

Each part of  $dU$  above is experimentally observable

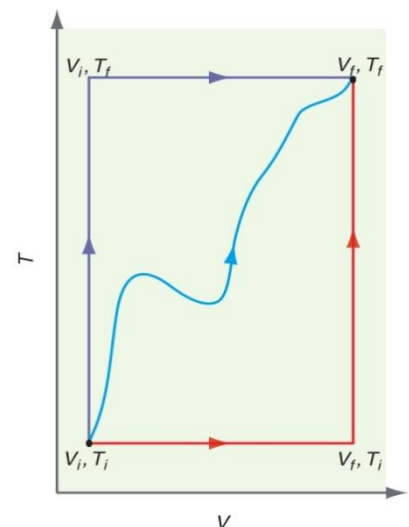
Alternatively: If have a process can break up into simpler steps and evaluate state functions, sum for state change: e.g. const  $T$

$$dU = dU_T = [T(\partial P / \partial T)_V - P] dV$$

const  $V$

$$dU = dU_V = C_V dT$$

total is sum, path independent (do red or blue path)  $\rightarrow$



## Comparing dependence of U on T and V

Ideal gas,  $U = U(T)$ , but *real gas* interaction  $\rightarrow U(T, V)$

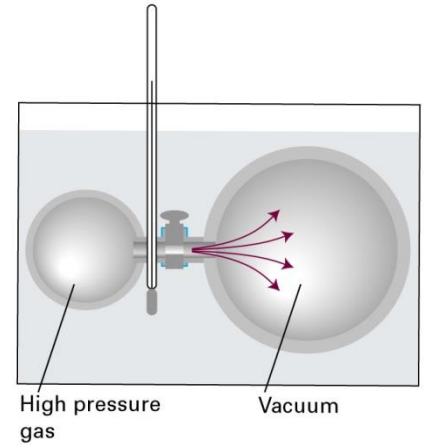
*Joule experiment* – expand gas into a vacuum,

heat from system to bath should be  $(\partial U/\partial V)$

since vacuum:  $p_{\text{ext}} = 0$ ,  $w = 0$ , so  $dU = dq = dU_V + dU_T$

*Joule result* - no change in T, so assume  $dT_{\text{sys}} = dT_{\text{sur}} = 0$  or

$dq = 0 \rightarrow (\partial U/\partial V)_T dV = 0$  since  $dV \neq 0 \rightarrow (\partial U/\partial V)_T = 0$



Joule experiment not sensitive enough, but observation does fit ideal behavior (above), later with Thomson they got more sensitive  $\rightarrow (\partial U/\partial V)_T \neq 0$  but very small

**Example:** For van der Waals gas:  $P = RT/(V_m - b) - a/V_m^2$  calculate  $(\frac{\partial U}{\partial V})_T = T(\frac{\partial P}{\partial T})_V - P$   
And determine  $\Delta U_{Tm} = \int (\partial U/\partial V)_T dV_m$  from  $V_m^i$  to  $V_m^f$

a.  $\pi_T = T(\partial U/\partial V)_V - P = T[R/(V_m - b)] - P = RT/(V_m - b) - [RT/(V_m - b) - a/V_m^2] = a/V_m^2$

b.  $\Delta U_{Tm} = \int (\partial U/\partial V)_T dV_m = \int a/V_m^2 dV = -a(1/V^f - 1/V^i) \rightarrow$  expansion,  $1/V^i > 1/V^f$ ,  $\Delta U_{Tm} (+)$

So change in U depends on a, the interaction term in van der Waals model

Relative size of  $dU_T = (\partial U/\partial V)_T$  and  $dU_V = (\partial U/\partial T)_V$

**Example:** expand  $N_2$  from ( $T=200\text{K}$ ,  $P=5.0\text{ bar}$ ) to ( $T=400\text{ K}$ ,  $P=20\text{ bar}$ ),

$a = 0.137\text{ Pa}\cdot\text{m}^6\text{mol}^{-2}$ ,  $b = 3.87 \times 10^{-5}\text{ m}^3\text{mol}^{-1}$ ,  $C_{Vm} = (22.5 - 1.2 \times 10^{-2}T + 2.4 \times 10^{-5}T^2)\text{ JK}^{-1}\text{mol}^{-1}$

solution can be done by breaking into const V step and const T step, find:

$\Delta U_T = -132\text{ Jmol}^{-1}$  and  $\Delta U_V = 4.17\text{ kJmol}^{-1} \rightarrow dU_T = (\partial U/\partial V)_T$  much smaller (~3%)

Good *approximation* for gasses assume:  $\Delta U \sim \Delta U(T)$  or  $\Delta U_T = \int (\partial U/\partial V)_T dV \sim 0$

Solids and liquids, moderate conditions,  $V_m = 1/\rho \sim \text{const}$ , or  $dV_m \sim 0$

So  $\Delta U_{Tm} = \int (\partial U/\partial V)_T dV \sim (\partial U/\partial V)_T \Delta V \sim 0$ , which is independent of  $(\partial U/\partial V)_T$

Result means in most cases:  $\Delta U = U^f(T, V) - U^i(T, V) = \int C_V dT$  (but not only const. V)

Note: assumes no phase changes, no chemical reactions (these come later!)

## Enthalpy and constant Pressure processes

Let  $P = P_{\text{ext}}$  (const) :  $dU = dq_P - PdV$  integrate  $U^f - U^i = q_P - P(V^f - V^i) \rightarrow$

$(U^f - PV^f) - (U^i - PV^i) = q_P$  so if  $H = U + PV$  then  $\Delta H = q_P \rightarrow$  independent

$\rightarrow$  any process, const P, closed system, only P-V work

*Fusion and vaporization*, need heat to overcome molecular interaction, form new phase

$\Delta H = q_P > 0$ ,  $\Delta U_{\text{vap}} = \Delta H_{\text{vap}} - P\Delta V_{\text{vap}} > 0$  ----  $\Delta V_{\text{vap}} \gg 0$ , so  $\Delta U_{\text{vap}} < \Delta H_{\text{vap}}$

By contrast,  $\Delta V_{\text{fus}}$  small, so  $\Delta U_{\text{fus}} \sim \Delta H_{\text{fus}}$



like before:  $dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$  for const P,  $dP = 0$ ,  $\delta q_P = \left(\frac{\partial H}{\partial T}\right)_P dT$

so we again get heat capacity at const P:  $C_P = (\partial H/\partial T)_P$

extensive, so use  $C_{P,m}$ , H state variable, so evaluate by  $\Delta H_P = \int C_P dT$

relationship works for all systems, if there is no reaction or phase change

Relate  $C_V$  and  $C_P$  – from  $dH = dU + d(PV) = \delta q_P = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + P dV$

Const P:

but  $dq_P = C_P dT$ , so “divide through” by  $dT$ , combine terms in  $(\partial V/\partial T)_P$

$$C_P = C_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P = C_V + \left[ \left(\frac{\partial U}{\partial V}\right)_T + P \right] \left(\frac{\partial V}{\partial T}\right)_P$$

Use  $\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P$   
 then cyclic rule  
 $(\partial P/\partial T)_V = -1/(\partial V/\partial P)_T (\partial T/\partial V)_P$   
 $= -(\partial V/\partial T)_P / (\partial V/\partial P)_T$

$$C_P = C_V + T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P = C_V - T \frac{\left(\frac{\partial V}{\partial T}\right)_P^2}{\left(\frac{\partial V}{\partial P}\right)_T}$$

and definitions of  $\beta$  ( $\alpha$  – Atkins) and  $\kappa$ :

So  $C_P$  and  $C_V$  for any substance or phase, can be related by knowing only  $V_m$ ,  $\kappa$  and  $\beta$

$$C_P = C_V + TV \frac{\beta^2}{\kappa} \quad \text{or} \quad C_{P,m} = C_{V,m} + TV_m \frac{\beta^2}{\kappa}$$

Ideal gas,  $(\partial U/\partial V)_T = 0$ , and  $P(\partial V/\partial T)_T = P(nR/P) = nR$ , so  $C_P - C_V = nR$

For solids and liquids  $(\partial V/\partial T)_P = V\beta$  and is *much smaller*, so  $C_V \gg \left[ \left(\frac{\partial U}{\partial V}\right)_T + P \right] \left(\frac{\partial V}{\partial T}\right)_P$   
 $C_P \sim C_V \rightarrow$  solid and liquid heat capacities measure at const P, not easy to control V

### Enthalpy with pressure at const T

Same as above for  $dU$ , full variation for  $d(PV)$ :

$$dH = dU + d(PV) = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + V dP + P dV$$

$$dH = C_V dT + \left[ \left(\frac{\partial U}{\partial V}\right)_T + P \right] dV + V dP$$

Often  $(\partial H/\partial T)_P dT \gg (\partial H/\partial P)_T dP$  so ignore P dependence, but need for refrigerator

divide through above by  $dP$ , then  $(\partial H/\partial P)_T \rightarrow$  isothermal,  $dT = 0$ , 1<sup>st</sup> term  $(C_V dT) = 0$ ,

$$\left(\frac{\partial H}{\partial P}\right)_T = \left[ \left(\frac{\partial U}{\partial V}\right)_T + P \right] \left(\frac{\partial V}{\partial P}\right)_T + V$$

Rearrange using  $(\partial U/\partial V)_T = T(\partial P/\partial T)_V - P$ , so two P's cancel in bracket, and then use cyclic rule:  $(\partial P/\partial T)_V (\partial V/\partial P)_T = -1/(\partial T/\partial V)_P = (\partial V/\partial T)_P = \beta V$

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

So **P dependence of H is V**, corrected by  $\beta$  expansion coefficient, ideal is  $(\partial H/\partial P)_T = 0$   
 Recall ideal:  $\beta = (\partial V/\partial T)_P/V = (\partial(RT/P)/\partial T)_P/V = R/PV = 1/T$

Real gases  $(\partial H/\partial P)_T \neq 0$ , and important for heat transfer (**refrigerator** – expand gas, extract heat from “system” and then recompress, dump heat to “surrounding” → kitchen!)  
 Solids and liquids,  $(\partial V/\partial P)_T$  very small, so  $(\partial H/\partial P)_T \sim V$ , and  $dH = C_p dT + V dP$

**Example:** Calculate  $\Delta H$  for 124 g liquid MeOH at 1.0 bar and 298 K

change to 2.5 bar and 425 K,  $\rho = 0.79 \text{ g cm}^{-3}$  and  $C_{Pm} = 81 \text{ JK}^{-1} \text{ mol}^{-1}$

Choose const T path follow with const V path, use above result for dH liquid

$$\Delta H = n \int C_{Pm} dT + \int V dP \sim n C_{Pm} \Delta T + V \Delta P$$

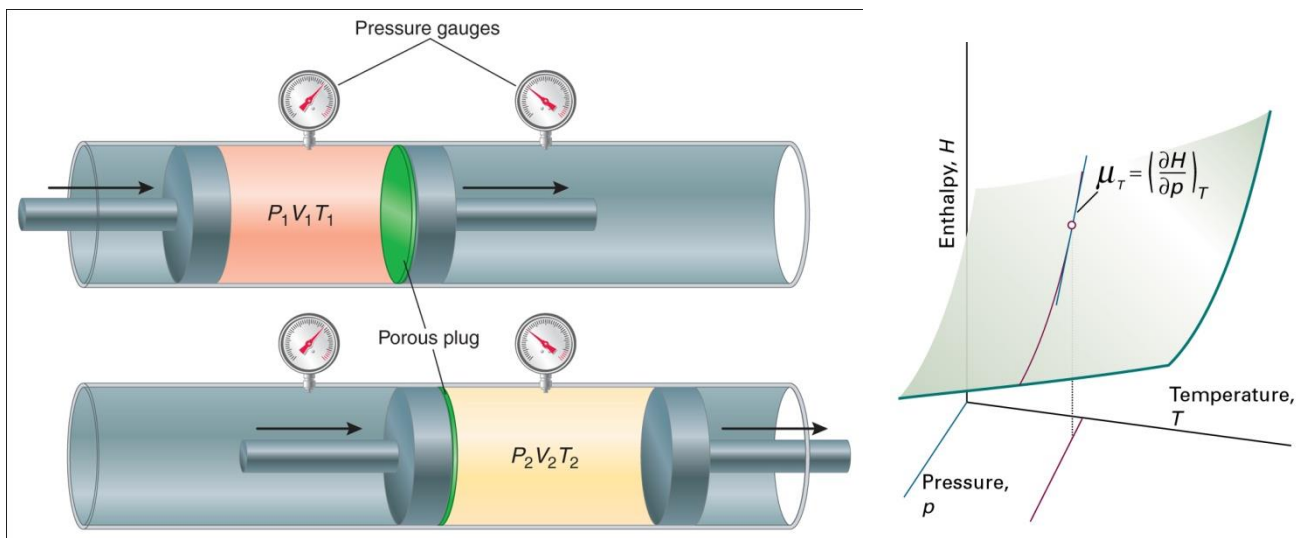
$$= 81 \text{ JK}^{-1} \text{ mol}^{-1} (124 \text{ g} / 32 \text{ g mol}^{-1}) 127 \text{ K} + (124 \text{ g} / 0.79 \text{ g cm}^{-3}) 10^{-6} \text{ m}^3 \text{ cm}^{-3} \times 1.5 \times 10^5 \text{ Pa}$$

$$= 39.9 \times 10^3 \text{ J} + 23.5 \text{ J} \sim 40 \text{ kJ} \quad \text{- first term, heat capacity, dominates, P depend. small}$$

### Joule Thomson Effect

Expand a gas, e.g. open an  $\text{N}_2$  cylinder,  $\Delta P \gg 0$ , see nozzle get cold (typical)

**Model system:** Gas transferred from high to low pressure through porous plug, isolated cylinder, piston moves to keep P values const,  $\Delta P=0$ , V and T both changing



Changes are determined by gas property, e.g.  $\text{N}_2$  cools as expands,  $P_1 > P_2$  and  $T_1 < T_2$

$$w_{\text{tot}} = w_{\text{lt}} + w_{\text{rt}} = - \int P_1 dV - \int P_2 dV = P_1 V_1 - P_2 V_2 \quad (\text{recall start } V_1 \rightarrow 0 \text{ and other side } 0 \rightarrow V_2)$$

$$\text{adiabatic, } q = 0, \Delta U = w = U_1 - U_2 = P_1 V_1 - P_2 V_2, \text{ rearrange: } U_1 + P_1 V_1 = U_2 + P_2 V_2$$

$$\rightarrow H_1 = H_2 \quad \text{isoenthalpic, here } dP \text{ and } dT \text{ negative, so } (\partial T/\partial P)_H > 0$$

Joule Thomson coefficient:  $\mu_{J-T} = \lim_{\Delta P \rightarrow 0} \left( \frac{\Delta T}{\Delta P} \right)_H = \left( \frac{\partial T}{\partial P} \right)_H$

For isenthalpic:  $dH = C_p dT + \left( \frac{\partial H}{\partial P} \right)_T dP = 0$  divide by dP, rearrange:

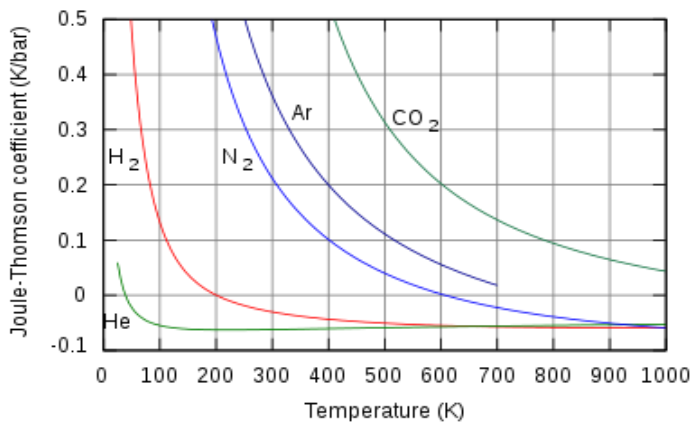
$$C_p \left( \frac{\partial T}{\partial P} \right)_H + \left( \frac{\partial H}{\partial P} \right)_T = 0 \text{ giving } \left( \frac{\partial H}{\partial P} \right)_T = -C_p \mu_{J-T}$$

So  $(\partial H/\partial P)_T$  can be measured knowing  $C_p$  and  $\mu_{JT}$  both of which depend on material

Define:  $\mu_T = (\partial H/\partial P)_T = -C_p \mu_{JT}$  as *isothermal Joule-Thomson coefficient*

As before  $\mu_{JT} = 0$  for ideal gas, but for van der Waals, as  $P \rightarrow 0$ ,  $\mu_{JT} = (2a/RT - b)/C_{pm}$

Some example values and temperature variation from Web



From above  $\mu_{JT} = (\partial H/\partial P)_T / C_p$

Which can be shown to be:

$$\mu_{JT} = \left( \frac{\partial T}{\partial P} \right)_H = \frac{V}{C_p} (\alpha T - 1)$$

where  $\alpha$  – thermal expansion

[or  $\beta = (\partial V/\partial T)_P / V$ ]

Note:  $\mu_{JT}$  (+) cools on expand

Example: solve  $\mu_{JT}$  for van der Waals gas

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

evaluate  $(\partial P/\partial T)_{\bar{V}}$  and  $(\partial P/\partial \bar{V})_T$ :

$$\left( \frac{\partial P}{\partial T} \right)_{\bar{V}} = \frac{R}{\bar{V} - b}$$

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

$$\mu_{JT} = \frac{1}{C_p} \left[ -T \frac{\left( \frac{\partial P}{\partial T} \right)_{\bar{V}}}{\left( \frac{\partial P}{\partial \bar{V}} \right)_T} - \bar{V} \right]$$

$$= \frac{1}{C_p} \left[ -T \frac{\left( \frac{R}{\bar{V} - b} \right)}{-\frac{RT}{(\bar{V} - b)^2} + 2\frac{a}{\bar{V}^3}} - \bar{V} \right]$$

$$= \frac{1}{C_p} \left[ \frac{1}{\frac{1}{(\bar{V} - b)} - 2\frac{\bar{V} - b}{RT} \frac{a}{\bar{V}^3}} - \bar{V} \right]$$

Take limit of large molecular volume:

*Expansion tricky, find common denom.*

$$\lim_{\bar{V} \rightarrow \infty} \mu_{JT} = \frac{1}{C_p} \lim_{\bar{V} \rightarrow \infty} \left[ -T \frac{\left( \frac{R}{\bar{V} - b} \right)}{-\frac{RT}{(\bar{V} - b)^2} + 2\frac{a}{\bar{V}^3}} - \bar{V} \right]$$

$$= \frac{1}{C_p} \lim_{\bar{V} \rightarrow \infty} \left[ -\bar{V} \frac{(-2ab^2 + 4ab\bar{V} - 2a\bar{V}^2 + bRT\bar{V}^2)}{-2ab^2 + 4ab\bar{V} - 2a\bar{V}^2 + RT\bar{V}^3} \right]$$

$$= \frac{1}{C_p} \left[ \frac{2a}{RT} - b \right]$$