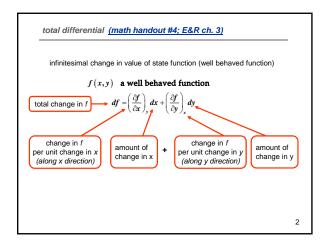
Chemistry 163B

Lecture 5 Winter 2014

Challenged Penmanship

Notes

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differential of product (product rule)

$$d(xy) = ydx + xdy$$

3

example of implication of total differentials

First Law

$$dU_{sys} = dq_{sys} + dw_{sys} + dn_{sys} \text{ (n=number of moles; dn=0 for closed system)}$$

$$U \text{ is state function} \Rightarrow dU_{sys} \text{ is exact differential}$$

$$dn = 0 \text{ (closed system)}$$

$$dU(T, P) = \left(\frac{\partial U}{\partial T}\right)_p dT + \left(\frac{\partial U}{\partial P}\right)_T dP \stackrel{first law}{=} dq_{sys} + dw_{sys}$$

$$OR$$

$$dU(T, V) = \left(\frac{\partial U}{\partial T}\right)_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV \stackrel{first law}{=} dq_{sys} + dw_{sys}$$
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"divide through by ??"

#### math handout <u>#</u>6

$$dU(T, P) = \left(\frac{\partial U}{\partial T}\right)_{P} dT + \left(\frac{\partial U}{\partial P}\right)_{T} dP$$

"divide through by dV holding x (something else) constant "

$$\left(\frac{\partial U}{\partial V}\right)_X = \left(\frac{\partial U}{\partial T}\right)_P \left(\frac{\partial T}{\partial V}\right)_X + \left(\frac{\partial U}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_X$$

later special simplification if x=P or T

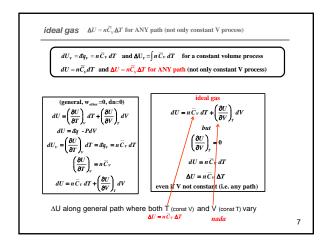
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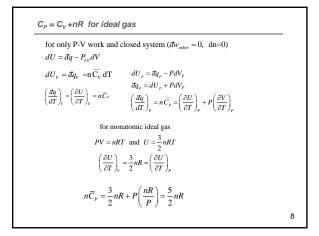
two relationships for ideal gasses: a ( $_{U}$ /sec) look ahead (will prove rigorously in next lecture, but gthis is the next lecture)

• for any substance  $dU_v = dq_v = n\bar{C}v dT$  and  $\Delta U_v = [n\bar{C}v dT]$  for a constant volume process

• but for an ideal gas  $dU = n\bar{C}_v dT$  and  $\Delta U = n\bar{C}_v \Delta T$  for ANY path (not only constant V process) [other parts of path, changes of P and V with constant T, give zero contribution to AU]

• for ideal gas  $\bar{C}_p = \bar{C}_v + R$ • monatomic ideal gas  $\bar{C}_v = \frac{3}{2}R \quad \bar{C}_p = \frac{5}{2}R$ [simple proof coming soon]





 $U \equiv \text{internal energy} \\ dU_{sys} = dq_{sys} + dw_{sys} + dn_{sys} \text{ (n=number of moles; dn=0 for closed system)} \\ dU_{sys} = -dU_{uur} \text{ (energy conserved)} \\ dU \text{ is exact differential} \\ U \text{ is a state function} \text{ completely general} \\ \\ \text{for only P-V work and closed system (dn=0)} \\ dU = dq - P_{ex} dV \\ \text{ • Constant volume process } dU_{V} = dq_{V} \quad \Delta U_{V} = q_{V} \\ \text{ • Adiabatic process} \qquad dU = dw \quad \Delta U = w \\ \\ 9$ 

enthalpy: q for process at constant Pressure  $H\equiv U+P_{\rm int}V \qquad (\text{definition of enthalpy, H})$  since U is state function and P, V are state variables, H is also a  $\text{STATE FUNCTION} \qquad \textit{completely general}$  why a new state function you might ask??  $dU_V = dq_V \quad ; \quad \Delta U_V = q_V \quad \textit{heat at constant volume}$  but most reactions and many physical processes are carried out at constant P  $\text{desire state function for } \mathbf{q_P}, \text{ heat at constant pressure}$ 

enthaply: H, a state function for heat transfer at constant pressure  $H \equiv U + P_{\text{int}}V$  dH = dU + PdV + VdP  $dH = dq - PdV + dw_{\text{other}} + PdV + VdP$   $dH = dq + VdP + dw_{\text{other}}$ and at P=constant and  $dw_{\text{other}} = 0$   $dH_P = dq_P$   $\Delta H_P = q_P \text{ as advertised !!}$   $\Delta H_P = q_P \text{ at const P no w}_{\text{other}}$   $\Delta H_P > 0 \text{ endothermic (heat gained by system)}$   $\Delta H_P < 0 \text{ exothermic (heat lost by system)}$ 

 $\Delta H_P = q_p = \int n \bar{C}_P dT \approx n \bar{C}_P \Delta T \quad \text{(general, } \mathbf{w}_{\text{other}} = 0, \text{ dn} = 0\text{)}$  ideal gas H = U + PV = U + nRT  $dH = dU + nRdT \quad \text{(general for ideal gas)}$   $dH = n\bar{C}_p dT + nRdT \quad \text{(general for ideal gas, even V not const)}$   $dH = n(\bar{C}_p + R) dT$   $dH = n(\bar{C}_p + R) dT$   $dH = n(\bar{C}_p \Delta T \quad \text{iDEAL GAS ANYTIME,}$  EVEN IF P NOT CONSTANT  $\Delta H = n(\bar{C}_p \Delta T \quad \text{ideal gas general (} \mathbf{w}_{\text{other}} = 0, \text{ dn} = 0\text{)}$ 

manipulating thermodynamic functions: fun and games

for example:

HW#3

12. Derive the following for any closed system, with only P-V work:

$$C_{V} = -\left(\frac{\partial U}{\partial V}\right)_{T} \left(\frac{\partial V}{\partial T}\right)_{U}$$

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total differential for U(T,V,n) and H(T,P,n)

$$\begin{split} &U(T, V, n_1, n_2, ..., n_N) \\ &dU = \left(\frac{\partial U}{\partial T}\right)_{V,n} dT + \left(\frac{\partial U}{\partial V}\right)_{T,n} dV + \sum_{i=1}^{N} \left(\frac{\partial U}{\partial n_i}\right)_{T, V, n_i \neq n_i} dn_i \end{split}$$

$$H(T,P,n_1,n_2,...,n_N)$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_{P,n} dT + \left(\frac{\partial H}{\partial P}\right)_{T,n} dP + \sum_{i=1}^{N} \left(\frac{\partial H}{\partial n_{i}}\right)_{T,P,n_{i} \neq n_{i}} dn_{i}$$

for now closed system all dn;=0

1/

H(T,P): some manipulations and relationships (closed system)

dH = dq + VdP closed system,  $dw_{ather} = 0$ 

'divide by dT, holding P constant'  $\left(\frac{\partial H}{\partial T}\right)_{p} = \left(\frac{dq}{dT}\right)_{p} + V\left(\frac{\partial P}{\partial T}\right)_{p}$  math handout #6

 $\left( \frac{\partial T}{\partial T} \right)_P \left( \frac{\partial T}{\partial T} \right)_P = \left( \frac{dq}{dT} \right)_P = n \, \bar{C}_P$ 

'divide by dP, holding T constant'

$$\left(\frac{\partial H}{\partial P}\right)_{T} = \left(\frac{dq}{dP}\right)_{T} + V\left(\frac{\partial P}{\partial P}\right)_{T}$$

$$\left(\frac{\partial H}{\partial P}\right)_{-} = \left(\frac{dq}{dP}\right)_{-} + V$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_{-} dT + \left(\frac{\partial H}{\partial P}\right)_{-} dP$$

 $dH = n\overline{C}_p dT + \left(\frac{\partial H}{\partial P}\right)_T dP \qquad \text{eqns. 3.30-3.32 E\&R (p. 56 [52]_{2d})}$ 

U(T,V): some manipulations and relationships (closed system)

dU = dq - PdV closed system,  $dw_{other} = 0$ 

'divide by dT, holding V constant'

$$\left(\frac{\partial U}{\partial T}\right)_{V} = \left(\frac{dq}{dT}\right)_{V} - P\left(\frac{\partial V}{\partial T}\right)_{V}$$

$$\left(\frac{\partial U}{\partial T}\right)_{v} = \left(\frac{dq}{dT}\right)_{v} = n\,\bar{C}_{v}$$

'divide by dV, holding T constant'

$$\left(\frac{\partial U}{\partial V}\right)_{T} = \left(\frac{dq}{dV}\right)_{T} - P\left(\frac{\partial V}{\partial V}\right)_{T}$$

$$\left(\frac{\partial U}{\partial V}\right)_{T} = \left(\frac{dq}{dV}\right)_{T} - P$$

$$dU = \left(\frac{\partial U}{\partial T}\right) dT + \left(\frac{\partial U}{\partial V}\right) dV$$

$$dU = n\overline{C}_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \qquad \text{eqn. 3.12-3.15 E&R (p 50 [46]_{2a})}$$

save for later when we have tools from 2<sup>nd</sup> Law of Thermodynamics

$$dU = n\overline{C}_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$
 need 2<sup>nd</sup> Law to evaluate this in terms of P,V,T

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P \quad E \& R \quad eqn.3.19$$

many of the results in E&R ch 3 use this [yet] 'unproven' result; we will derive later class should use result in HW3 #13\* some important relationships between C<sub>P</sub> and C<sub>V</sub>

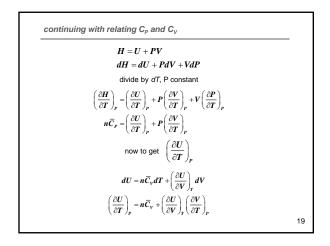
$$\frac{1}{n} \left( \frac{\partial H}{\partial T} \right)_{n} = \bar{C}_{p}$$
 and  $\frac{1}{n} \left( \frac{\partial U}{\partial T} \right)_{v} = \bar{C}_{v}$ 

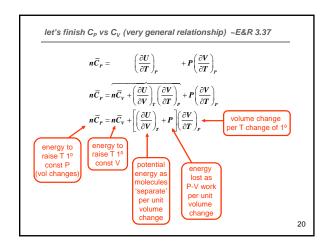
to get relationship between  $C_P$  and  $C_V$  one needs to have relationship involving both H and U; soooo

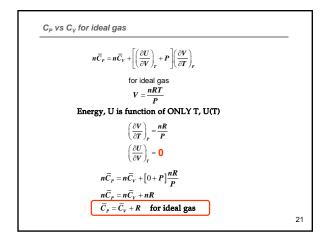
$$H = U + PV$$

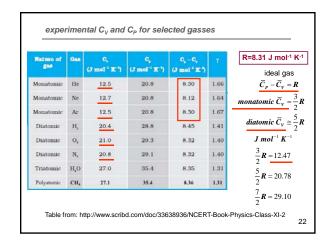
$$dH = dU + PdV + VdP$$

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in section derive equation following equation  $n \overline{C}_v = n \overline{C}_r + \left[ \left( \frac{\partial H}{\partial P} \right)_r - V \right] \left( \frac{\partial P}{\partial T} \right)_v$  start with dU = dH - PdV - VdP divide by dT with V constant and then boogie along as we just did!!

