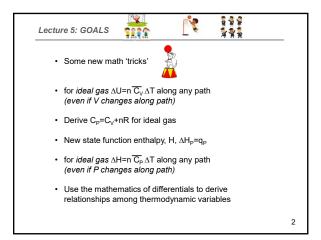
Chemistry 163B

Lecture 5 Winter 2020

Mathematics for Thermodynamics
Enthalpy

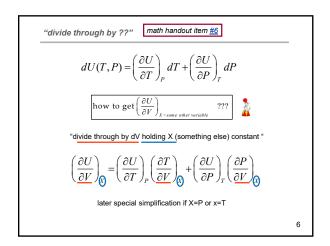
Challenged Penmanship Notes

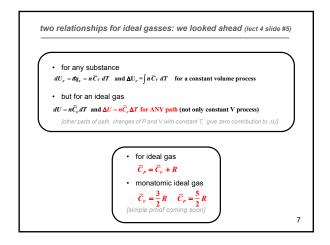


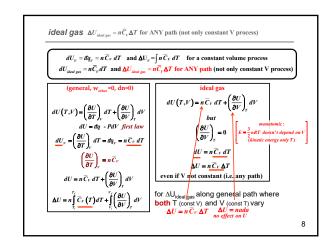
infinitesimal change in value of state function (well behaved function) $f(x,y) \quad \text{a well behaved function}$ $total change in f \qquad df = \left(\frac{\partial f}{\partial x}\right)_x dx + \left(\frac{\partial f}{\partial y}\right)_x dy$ $change in f \qquad change in x \\ (along x direction) \qquad amount of \\ change in x \qquad direction) \qquad amount of \\ change in y \qquad direction) \qquad amount of \\ change in y \qquad direction)$

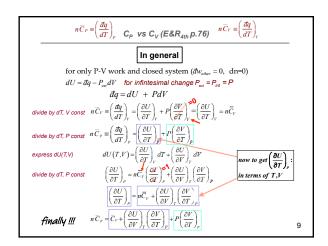
d(xy) = ydx + xdy

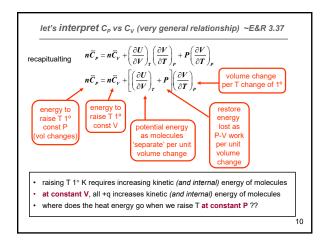
First Law $dU_{ys} = dq_{ys} + dw_{ys} + dn_{ys} \text{ (n=number of moles; dn=0 for closed system)}$ $U \text{ is state function } \Rightarrow dU_{qs} \text{ is exact differential}$ $dU(\underline{T,P}) = \begin{pmatrix} \partial U \\ \partial T \end{pmatrix}_{p} \frac{dT}{dT} + \begin{pmatrix} \partial U \\ \partial P \end{pmatrix}_{T} \frac{dP}{dT} = dq_{ys} + dw_{ys}$ OR $dU(\underline{T,V}) = \begin{pmatrix} \partial U \\ \partial T \end{pmatrix}_{p} \frac{dT}{dT} + \begin{pmatrix} \partial U \\ \partial V \end{pmatrix}_{T} \frac{dV}{dT} = dq_{ys} + dw_{ys}$ 5

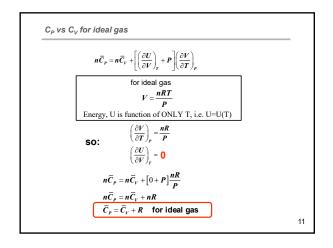


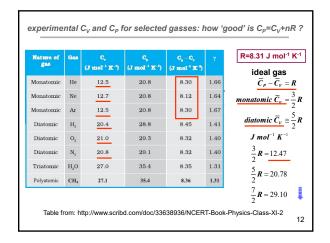












1st Law recapitulation U ≡ internal energy $dU_{sys} = dq_{sys} + dw_{sys} + dn_{sys}$ (n=number of moles; dn=0 for closed system) $dU_{sys} = -dU_{surr}$ (energy conserved) dU is exact differential U is a state function completely general for only P-V work and closed system (dn=0) $dU = dq - P_{ext}dV$ • Constant volume process $dU_v = dq_v \Delta U_v = q_v$ Adiabatic process dU = dw $\Delta U = w$ 13

enthalpy: q for process at constant Pressure H≡U+P_{int}V (definition of enthalpy, H) since U is state function; and since P, V are state variables, H is also a STATE FUNCTION completely general why a new state function you might ask?? $dU_v = dq_v$; $\Delta U_v = q_v$ heat at constant volume but most reactions and many physical processes are carried out at constant P desire state function for $\mathbf{q}_{\mathbf{p}}$, heat at constant pressure

enthaply: H, a state function for heat transfer at constant pressure $H \equiv U + P_{in}V$ dH = dU + PdV + VdP $(P_{ii} = P_{cit} \text{ for infinitesimal change dP})$ $dH = dq - PdV + dw_{other} + PdV + VdP$ $dH = dq + VdP + dW_{other}$ and at P=constant and $dw_{other} = 0$ $dH_p = dq_p$ $\Delta H_P = q_P$ as advertised!! $\Delta H_P = q_P$ at const P and no \mathbf{w}_{other} $\Delta H_P > 0$ endothermic (heat gained by system) $\Delta H_P < 0$ exothermic (heat lost by system) 15 ∆H ideal gas $\Delta H_P = q_p = \int n \overline{C}_P dT \approx n \overline{C}_P \Delta T \quad \text{(general, for } w_{\text{obs}} = 0, \, \text{dn} = 0)$ but for ideal gas $H \equiv U + PV = U + nRT$ dH = dU + nRdT (general for ideal gas) $dH = n\overline{C}_v dT + nRdT$ (general for ideal gas, even V not const) $dH = n(\overline{C}_v + R)dT$ $dH = n\overline{C}_{p}dT$ IDEAL GAS ANYTIME, EVEN IF P NOT CONSTANT $\Delta H = n \overline{C}_p \Delta T$ ideal gas general (for $w_{other} = 0$, dn=0) 16

manipulating thermodynamic functions: fun and games

GOALS:

Evaluate chang adynamic functions in terms of se

thermodynamic €.g. ΔU, ΔH, etc) into expressions that can be evaluated in terms of P,V,T or other directly measurable quantities.

manipulating thermodynamic functions: fun and games

for example:

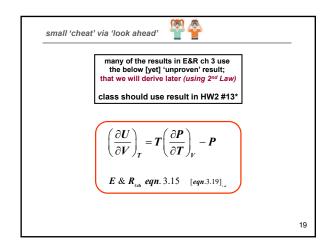
HW#2

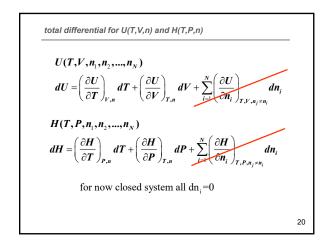
17

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

$$C_V = -\left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_U$$

18





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

$$dU(T,V) = \left(\frac{\partial U}{\partial T}\right)_{r} dT + \left(\frac{\partial U}{\partial V}\right)_{r} dV \quad closed \ system, \ \overline{d}w_{onc} = 0$$

$$dU(T,V) = dq - PdV$$

$$definition \ of \ \mathbf{C}_{V}: \quad \left(\frac{\partial U}{\partial T}\right)_{r} = \left(\frac{dq}{dT}\right)_{r} = C_{r} = n\overline{C}_{r}$$

$$\text{'divide dU by dV,} \quad holding \ \mathsf{T} \ constant': \quad \left(\frac{\partial U}{\partial V}\right)_{T} = \left(\frac{dq}{dV}\right)_{T} - P$$

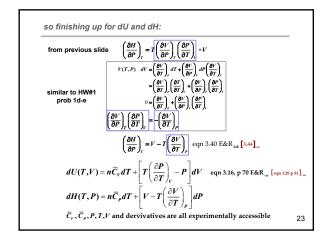
$$but \ here \ we \ can \ also \\ use \ our' \ look \ ahead': \quad \left(\frac{\partial U}{\partial V}\right)_{T} = T\left(\frac{\partial P}{\partial T}\right)_{r} - P$$

$$to \\ get$$

$$dU(T,V) = n\overline{C}_{r} dT + \left[T\left(\frac{\partial P}{\partial T}\right)_{r} - P\right] dV \quad \text{eqn } 3.16, p \ 70 \ \text{E&R}_{na} \ [\text{eqn } 3.20 \ \text{p Si}]_{loo}$$

$$\overline{C}_{r}, P, T, V \ \text{ and } \ dervivatives \ are \ all \ experimentally \ accessible}$$

$$H(T,P): some manipulations and relationships (closed system) \\ \hline (\partial H/\partial T)_p = C_P \qquad (\partial H/\partial P)_T = ?? \text{ in terms of P,V,T and derivatives} \\ dH(T,P) = \begin{pmatrix} \frac{\partial H}{\partial T} \end{pmatrix}_T dT + \begin{pmatrix} \frac{\partial H}{\partial P} \end{pmatrix}_T dP \\ and dH = dU + PdV + VdP \text{ closed system, } \partial V_{\infty} = 0 \\ \text{'divide dH by dP, holding T constant':} \qquad \begin{pmatrix} \frac{\partial H}{\partial P} \end{pmatrix}_T = \begin{pmatrix} \frac{\partial U}{\partial P} \end{pmatrix}_T + P \begin{pmatrix} \frac{\partial V}{\partial P} \end{pmatrix}_T + V \begin{pmatrix} \frac{\partial P}{\partial P} \end{pmatrix}_T \\ chain rule: \qquad \begin{pmatrix} \frac{\partial U}{\partial P} \end{pmatrix}_T = \begin{pmatrix} \frac{\partial U}{\partial V} \end{pmatrix}_T \begin{pmatrix} \frac{\partial V}{\partial P} \end{pmatrix}_T + V \begin{pmatrix} \frac{\partial V}{\partial P} \end{pmatrix}_T + V = \begin{pmatrix} \frac{\partial V}{\partial P} \end{pmatrix}_T \begin{pmatrix} \frac{\partial U}{\partial V} \end{pmatrix}_T + P \end{pmatrix} + V \\ \begin{pmatrix} \frac{\partial V}{\partial P} \end{pmatrix}_T - \begin{pmatrix} \frac{\partial V}{\partial P} \end{pmatrix}_T + \begin{pmatrix} \frac{\partial V}{\partial P} \end{pmatrix}_T + V = \begin{pmatrix} \frac{\partial V}{\partial P} \end{pmatrix}_T \begin{pmatrix} \frac{\partial U}{\partial V} \end{pmatrix}_T + P \end{pmatrix} + V \\ \begin{pmatrix} \frac{\partial V}{\partial P} \end{pmatrix}_T - \begin{pmatrix} \frac{\partial V}{\partial P} \end{pmatrix}_T + \begin{pmatrix} \frac{\partial V}{\partial P} \end{pmatrix}_T + V = \begin{pmatrix} \frac{\partial V}{\partial P} \end{pmatrix}_T \begin{pmatrix} \frac{\partial U}{\partial V} \end{pmatrix}_T + P \end{pmatrix} + V \\ \end{pmatrix} \text{ almost fini !!} \begin{pmatrix} \frac{\partial H}{\partial P} \end{pmatrix}_T = T \begin{pmatrix} \frac{\partial V}{\partial P} \end{pmatrix}_T \begin{pmatrix} \frac{\partial P}{\partial P} \end{pmatrix}_T + V \text{ eqn 3.40 E&R_{4a}} \begin{bmatrix} 3.44 \end{bmatrix}_{av} \end{pmatrix}$$



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

