Chemistry 163B

Lecture 5 Winter 2020

Mathematics for Thermodynamics
Enthalpy

Challenged Penmanship Notes
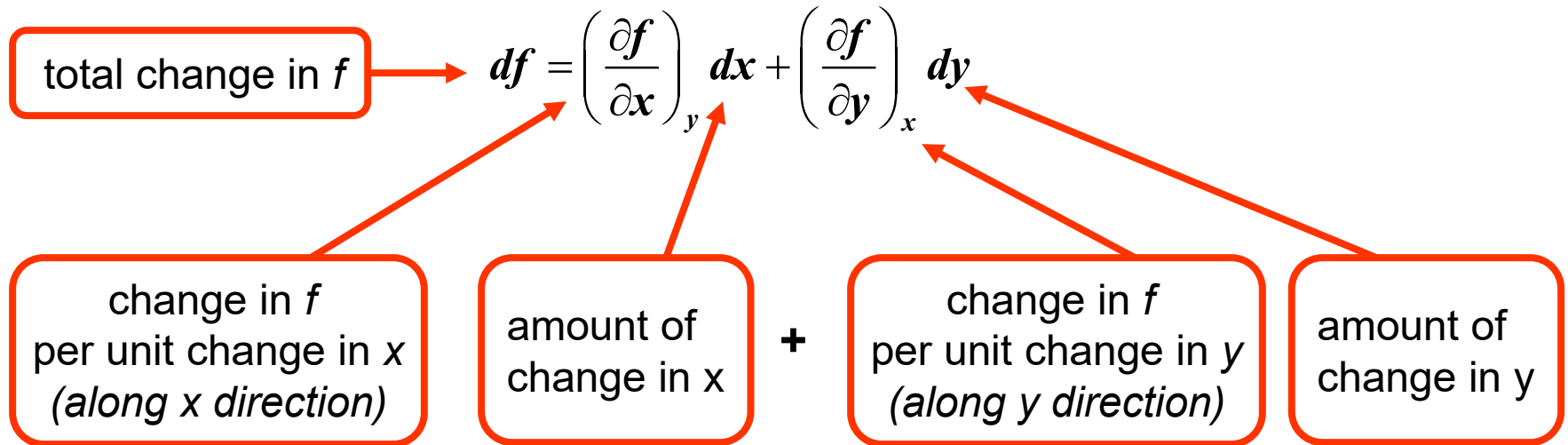
- Some new math 'tricks'

- for *ideal gas* $\Delta U = n \overline{C_V} \Delta T$ along any path
  (even if V changes along path)

- Derive $C_P = C_V + nR$ for ideal gas

- New state function enthalpy, H, $\Delta H_P = q_P$

- for *ideal gas* $\Delta H = n \overline{C_P} \Delta T$ along any path
  (even if P changes along path)

- Use the mathematics of differentials to derive relationships among thermodynamic variables

infinitesimal change in value of state function (well behaved function)

$f(x, y)$ **a well behaved function**

| total change in *f* | → | $$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$ |

change in *f*
per unit change in *x*
(along x direction)

amount of
change in x

+

change in *f*
per unit change in *y*
(along y direction)

amount of
change in y

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

example of implication of total differentials

First Law

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

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

for dn $= 0$ (closed system)

$$dU(T,P) \overset{math}{=} \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP \overset{first\ law}{=} \text{\dj}q_{sys} + \text{\dj}w_{sys}$$

OR

$$dU(T,V) \overset{math}{=} \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \overset{first\ law}{=} \text{\dj}q_{sys} + \text{\dj}w_{sys}$$

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

$$\text{how to get} \left(\frac{\partial U}{\partial V}\right)_{X=some\ other\ variable} \qquad ???$$

"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 x=T

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- for any substance

$$dU_V = đq_V = n\,\overline{C}_V\,dT \quad \text{and} \quad \Delta U_V = \int n\,\overline{C}_V\,dT \quad \textbf{for a constant volume process}$$

- but for an ideal gas

$$dU = n\overline{C}_V dT \quad \textbf{and} \quad \color{red}{\Delta U = n\overline{C}_V \Delta T} \textbf{ for ANY path} \textbf{ (not only constant V process)}$$

[other parts of path, changes of P and V with constant T, give zero contribution to ΔU]

- for ideal gas

$$\overline{C}_P = \overline{C}_V + R$$

- monatomic ideal gas

$$\overline{C}_V = \frac{3}{2}R \qquad \overline{C}_P = \frac{5}{2}R$$

[simple proof coming soon]

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ideal gas $\Delta U_{ideal\ gas} = n\overline{C}_V \Delta T$ **for ANY path (not only constant V process)**

$dU_V = đq_V = n\overline{C}_V\,dT$ **and** $\Delta U_V = \int n\overline{C}_V\,dT$ **for a constant volume process**

$dU_{ideal\ gas} = n\overline{C}_V dT$ **and** $\Delta U_{ideal\ gas} = n\overline{C}_V\Delta T$ **for ANY path (not only constant V process)**

(general, w_{other}=0, dn=0)

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

$$dU = đq - PdV \quad \textit{first law}$$

$$dU_V = \left(\frac{\partial U}{\partial T}\right)_V dT = đq_V = n\overline{C}_V\,dT$$

$$\left(\frac{\partial U}{\partial T}\right)_V \equiv n\overline{C}_V$$

$$dU = n\overline{C}_V\,dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$\Delta U = n\int_{T_i}^{T_f}\overline{C}_V(T)\,dT + \int_{V_i}^{V_f}\left(\frac{\partial U}{\partial V}\right)_T dV$$

ideal gas

$$dU(T,V) = n\overline{C}_V\,dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

but

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

$$\left[\begin{array}{l} \textit{monatomic:}\\ E = \frac{3}{2}nRT \ \textit{doesn't depend on V}\\ (\textit{kinetic energy only T}) \end{array}\right]$$

$$dU = n\overline{C}_V\,dT$$

$$\Delta U = n\overline{C}_V\,\Delta T$$

even if V not constant (i.e. any path)

for $\Delta U_{ideal\ gas}$ along general path where **both** T (const V) and V (const T) vary

$\Delta U = n\overline{C}_V\,\Delta T$ $\quad \Delta U = nada$
no effect on U

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$$n\overline{C}_P \equiv \left(\frac{đq}{dT}\right)_P \qquad C_P \text{ vs } C_V \text{ (E\&R}_{4th}\text{ p.76)} \qquad n\overline{C}_V \equiv \left(\frac{đq}{dT}\right)_V$$

In general

for only P-V work and closed system ($đw_{other} = 0$, dn=0)

$$dU = đq - P_{ext}dV \quad \text{for infintesimal change } P_{ext} = P_{int} = P$$

$$đq = dU + PdV$$

divide by dT, V const $\quad n\overline{C}_V \equiv \left(\frac{đq}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V + P\overset{=0}{\left(\frac{\partial V}{\partial T}\right)_V} = \left(\frac{\partial U}{\partial T}\right)_V = n\overline{C}_V$

divide by dT, P const $\quad n\overline{C}_P \equiv \left(\frac{đq}{dT}\right)_P = \boxed{\left(\frac{\partial U}{\partial T}\right)_P} + \boxed{P\left(\frac{\partial V}{\partial T}\right)_P}$

express dU(T,V) $\qquad dU(T,V) = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$
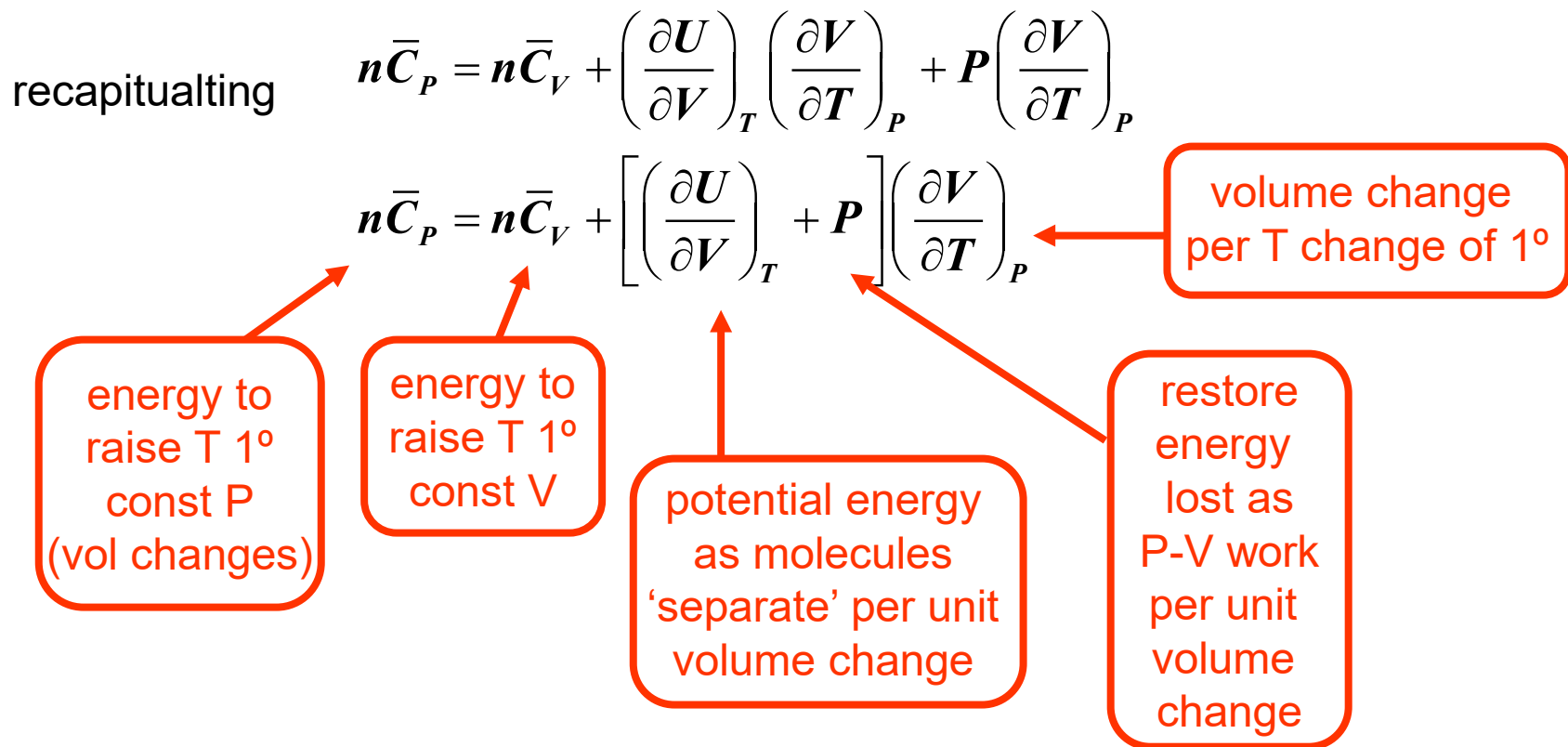
$\boxed{\begin{array}{l} \textbf{\textit{now to get}} \left(\dfrac{\partial U}{\partial T}\right)_P : \\[2mm] \textbf{\textit{in terms of T,V}} \end{array}}$

divide by dT, P const $\qquad \left(\frac{\partial U}{\partial T}\right)_P = n\overline{C}_V \overset{=1}{\left(\frac{\partial T}{\partial T}\right)_P} + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$

$$\boxed{\left(\frac{\partial U}{\partial T}\right)_P} = \boxed{n\overline{C}_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P}$$

finally !!! $\qquad n\overline{C}_P = \boxed{\overline{C}_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P} + \boxed{P\left(\frac{\partial V}{\partial T}\right)_P}$

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let's *interpret* C_P vs C_V (very general relationship) ~E&R 3.37

recapitualting

$$n\overline{C}_P = n\overline{C}_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

$$n\overline{C}_P = n\overline{C}_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P$$

volume change per T change of 1º

energy to raise T 1º const P (vol changes)

energy to raise T 1º const V

potential energy as molecules 'separate' per unit volume change

restore energy lost as P-V work per unit volume change

- raising T 1° K requires increasing kinetic *(and internal)* energy of molecules
- **at constant V**, all +q increases kinetic *(and internal)* energy of molecules
- where does the heat energy go when we raise T **at constant P** ??

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$$n\bar{C}_P = n\bar{C}_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P$$

for ideal gas

$$V = \frac{nRT}{P}$$

Energy, U is function of ONLY T, i.e. U=U(T)

so:

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = \mathbf{0}$$

$$n\bar{C}_P = n\bar{C}_V + [0 + P]\frac{nR}{P}$$

$$n\bar{C}_P = n\bar{C}_V + nR$$

$$\boxed{\bar{C}_P = \bar{C}_V + R \quad \textbf{for ideal gas}}$$

experimental C_V and C_P for selected gasses: how 'good' is $C_P = C_V + nR$?

Nature of gas	Gas	C_v (J mol^{-1} K^{-1})	C_p (J mol^{-1} K^{-1})	$C_p - C_v$ (J mol^{-1} K^{-1})	γ
Monatomic	He	12.5	20.8	8.30	1.66
Monatomic	Ne	12.7	20.8	8.12	1.64
Monatomic	Ar	12.5	20.8	8.30	1.67
Diatomic	H$_2$	20.4	28.8	8.45	1.41
Diatomic	O$_2$	21.0	29.3	8.32	1.40
Diatomic	N$_2$	20.8	29.1	8.32	1.40
Triatomic	H$_2$O	27.0	35.4	8.35	1.31
Polyatomic	CH$_4$	27.1	35.4	8.36	1.31

R=8.31 J mol^{-1} K^{-1}

ideal gas

$$\overline{C}_P - \overline{C}_V = R$$

$$\text{monatomic } \overline{C}_V = \frac{3}{2}R$$

$$\text{diatomic } \overline{C}_V \cong \frac{5}{2}R$$

$$J \; mol^{-1} \; K^{-1}$$

$$\frac{3}{2}R = 12.47$$

$$\frac{5}{2}R = 20.78$$

$$\frac{7}{2}R = 29.10$$

Table from: http://www.scribd.com/doc/33638936/NCERT-Book-Physics-Class-XI-2

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U ≡ internal energy

$dU_{sys} = đq_{sys} + đw_{sys} + dn_{sys}$ (n=number of moles; dn=0 for closed system)

$dU_{sys} = -dU_{surr}$ $\left(energy\ conserved \right)$

dU is exact differential

U is a state function   *completely general*

for only P-V work and closed system (dn=0)

$$dU = đq - P_{ext}dV$$

- **Constant volume process** $dU_V = đq_V$ $\Delta U_V = q_V$

- **Adiabatic process** $dU = đw$ $\Delta U = w$

$H \equiv U + P_{int}V$ (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??

$$dU_V = \bar{d}q_V \quad ; \quad \Delta U_V = q_V \quad \textit{heat at constant volume}$$

but most reactions and many physical processes are carried out at constant P

desire state function for q_P, heat at constant pressure

$$H \equiv U + P_{int}V$$

$$dH = \underline{dU} + PdV + VdP \qquad \left(P_{int} = P_{ext} \text{ for infinitesimal change } dP \right)$$

$$dH = \underline{đq - PdV + đw_{other}} + PdV + VdP$$

$$dH = đq + V\cancel{dP} + \cancel{đ}w_{other}$$

and at P=constant and $đw_{other} = 0$

$$dH_P = đq_P$$

$$\Delta H_P = q_P \quad \textbf{\textcolor{red}{as advertised !!}}$$

$\Delta H_P = q_P$ **at const P and no** w_{other}

$\Delta H_P > 0$ **endothermic (heat gained by system)**

$\Delta H_P < 0$ **exothermic (heat lost by system)**

ΔH ideal gas

$$\Delta H_P = q_p = \int n\overline{C}_P dT \approx n\overline{C}_P \Delta T \quad \text{(general, for } w_{other} = 0, dn = 0\text{)}$$

$$\boxed{\overline{C}_P \text{ independent of } T}$$

but for ideal gas

$$H \equiv U + PV = U + nRT$$

$$dH = dU + nRdT \quad \text{(general for ideal gas)}$$

$$dH = n\overline{C}_v dT + nRdT \quad \text{(general for ideal gas, even V not const)}$$

$$dH = n(\overline{C}_v + R)dT$$

$$dH = n\overline{C}_P dT \quad \text{IDEAL GAS ANYTIME,}$$

$$\text{EVEN IF P NOT CONSTANT}$$

$$\boxed{\Delta H = n\overline{C}_P \Delta T \quad \text{ideal gas general (for } w_{other} = 0, dn = 0\text{)}}$$

GOALS:

- Evaluate changes in thermodynamic functions in terms of selective constraints

  e.g. $\left(\dfrac{\partial V}{\partial T}\right)_U$

- Transform expressions for changes in thermodynamic functions (e.g. ΔU, ΔH, etc) into expressions that can be evaluated in terms of P,V,T or other directly measurable quantities.

for example:
HW#2

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

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

many of the results in E&R ch 3 use the below [yet] 'unproven' result;
that we will derive later *(using 2nd Law)*

class should use result in HW2 #13*

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

$E \& R_{4th} \ eqn. \ 3.15 \quad [eqn.3.19]_{3\,rd}$

$$U(T,V,n_1,n_2,...,n_N)$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_{V,n} dT + \left(\frac{\partial U}{\partial V}\right)_{T,n} dV + \sum_{i=1}^{N}\left(\frac{\partial U}{\partial n_i}\right)_{T,V,n_j \neq n_i} dn_i$$

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

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

for now closed system all $dn_i = 0$

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

$$dU(T,V) = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \qquad \textit{closed system, } \bar{d}w_{other} = 0$$

$$dU(T,V) = \bar{d}q - PdV$$

definition of C$_V$: $\quad \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\bar{d}q}{dT}\right)_V = C_V = n\bar{C}_V$

'divide dU by dV, holding T constant': $\quad \left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\bar{d}q}{dV}\right)_T - P$

$$\textit{hmmm } \left(\frac{\bar{d}q}{dV}\right)_T \overset{??}{=} T\left(\frac{\partial P}{\partial T}\right)_V \quad \textbf{see you later}$$

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

to get

$$\boxed{\begin{array}{l} dU(T,V) = n\bar{C}_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]dV \quad \text{eqn 3.16, p 70 E\&R}_{4th} \; [\text{eqn 3.20 p 51}]_{3rd} \\[2em] \bar{C}_V, P, T, V \text{ and derivatives are all experimentally accessible} \end{array}}$$

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

$$\left(\partial H / \partial T\right)_P = C_P \qquad \left(\partial H / \partial P\right)_T = ?? \ \text{in terms of P,V,T and derivatives}$$

start:

$$dH(T,P) = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

and

$$dH = dU + PdV + VdP \quad \textit{closed system, } đw_{other} = 0$$

'divide dH by dP, holding T constant':

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

chain rule:

$$\left(\frac{\partial U}{\partial P}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial P}\right)_T$$

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

using

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

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

almost fini !!

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_V + V \quad \text{eqn 3.40 E\&R}_{4th} \ [3.44]_{3rd}$$

so finishing up for dU and dH:

from previous slide

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

similar to HW#1 prob 1d-e

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

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

$$0 = \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_V$$

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

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P \quad \text{eqn 3.40 E\&R}_{4th}\; [3.44]_{3rd}$$

$$dU(T,V) = n\bar{C}_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]dV \quad \text{eqn 3.16, p 70 E\&R}_{4th}\; [\text{eqn 3.20 p 51}]_{3rd}$$

$$dH(T,P) = n\bar{C}_P dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]dP$$

$$\bar{C}_V, \bar{C}_P, P, T, V \text{ and derivatives are all experimentally accessible}$$

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$$n\overline{C}_V = n\overline{C}_P + \left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]\left(\frac{\partial P}{\partial T}\right)_V$$

start with

$$dU = dH - PdV - VdP$$

divide by dT **with V constant**

and then boogie along as we just did!!

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relationships that apply to **ideal gasses** for all conditions with $w_{other}=0$ and constant composition (some also apply **more generally**):

$\Delta U = q + w$	$w_{PV} = -\int P_{ext}dV$	$PV = nRT$
$q_V = n\int \overline{C}_V dT$ $\overset{?}{=} n\overline{C}_V \Delta T$	$q_P = n\int \overline{C}_P dT$ $\overset{?}{=} n\overline{C}_P \Delta T$	$\overline{C}_P = \overline{C}_V + R$
$H \equiv U + PV$	$\Delta U_{any\ conditions} = n\overline{C}_V \Delta T$	$\Delta H_{any\ conditions} = n\overline{C}_P \Delta T$
monatomic ideal gas	$\overline{C}_V = \frac{3}{2}R$	$\overline{C}_P = \frac{5}{2}R$

? only when C_v or C_p doesn't depend on T !

✓ Some new math 'tricks'

✓ for *ideal gas* $\Delta U = n \, \overline{C_V} \, \Delta T$ along any path *(even if V changes along path)*

✓ Derive $C_P = C_V + nR$ for ideal gas

✓ New state function enthalpy, H, $\Delta H_P = q_P$

✓ for *ideal gas* $\Delta H = n \, \overline{C_P} \, \Delta T$ along any path *(even if P changes along path)*

✓ Use the mathematics of differentials to derive relationships among thermodynamic variables

END OF LECTURE 5

why is C_V larger for diatomic than for monatomic gas ?

$$monatomic \; \overline{C}_V = \frac{3}{2}R$$

$$diatomic \; \overline{C}_V \cong \frac{5}{2}R$$

$$non-linear \; polyatomic \; \overline{C}_V > 3R$$

translational and rotational modes

each contribute $\frac{1}{2}$ **R to** $\overline{C}_V$

activated at high **T**
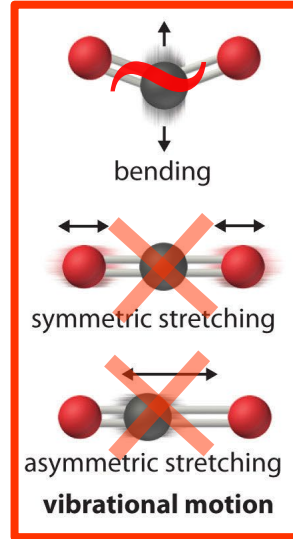
bending

symmetric stretching

asymmetric stretching

vibrational motion

rotational motion

translational motion
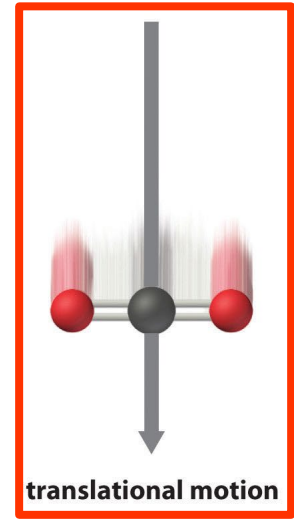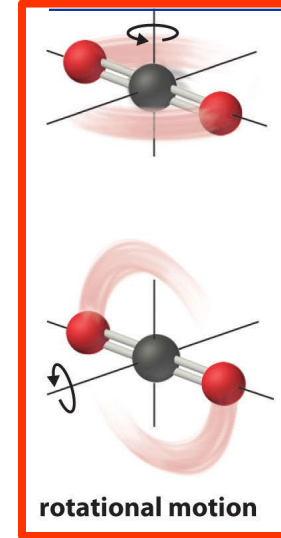
heat energy goes into	translation	rotation	vibration *active at 298K (total)*
monatomic	3	0	0 (0)
diatomic	3	2	0 (1)
polyatomic	3	3	>0 (3N-6)