# Chemistry 163B Winter 2020
## notes for lecture 5 Math and Enthalpy

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Chemistry 163B

Lecture 5 Winter 2020

Mathematics for Thermodynamics
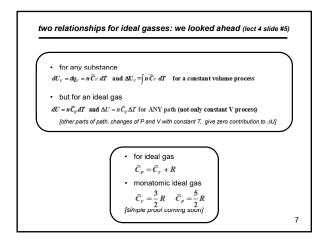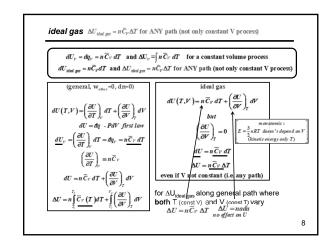Enthalpy

Challenged Penmanship Notes

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*Lecture 5: GOALS*

- 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
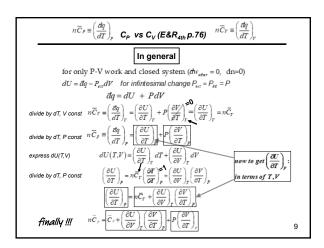  relationships among thermodynamic variables

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**total differential**  <u>*(math handout item #3; E&R ch. 3)*</u>

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

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

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

| 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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**differential of product (product rule)**

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

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**example of implication of total differentials**

First Law

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

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

⬇

*for dn = 0 (closed system)*

$dU\underline{(T,P)} \overset{exactly}{=} \left(\dfrac{\partial U}{\partial T}\right)_P dT + \left(\dfrac{\partial U}{\partial P}\right)_T dP \overset{first\,law}{=} đq_{sys} + đw_{sys}$

OR

$dU\underline{(T,V)} \overset{exactly}{=} \left(\dfrac{\partial U}{\partial T}\right)_V dT + \left(\dfrac{\partial U}{\partial V}\right)_T dV \overset{first\,law}{=} đq_{sys} + đw_{sys}$

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*"divide through by ??"*  | math handout item <u>#6</u>

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

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

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

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

later special simplification if X=P or x=T

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**two relationships for ideal gasses: we looked ahead** *(lect 4 slide #5)*

- for any substance

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

- but for an ideal gas

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

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

- for ideal gas
$$\bar{C}_P = \bar{C}_V + R$$
- monatomic ideal gas
$$\bar{C}_V = \frac{3}{2}R \quad \bar{C}_P = \frac{5}{2}R$$
*[simple proof coming soon]*

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

$$dU_V = dq_V = n\bar{C}_V\,dT \quad \text{and} \quad \Delta U_V = \int n\bar{C}_V\,dT \quad \text{for a constant volume process}$$
$$dU_{ideal\,gas} = n\bar{C}_V dT \quad \text{and} \quad \Delta U_{ideal\,gas} = n\bar{C}_V\Delta T \text{ for ANY path (not only constant V process)}$$

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

$$dU(T,V) = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$
$$dU = dq - PdV \quad \text{first law}$$
$$dU_V = \left(\frac{\partial U}{\partial T}\right)_V dT = dq_V = n\bar{C}_V\,dT$$
$$\left(\frac{\partial U}{\partial T}\right)_V = n\bar{C}_V$$
$$dU = n\bar{C}_V\,dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$
$$\Delta U = n\int_{T_1}^{T_2}\bar{C}_V(T)\,dT + \int_{V_1}^{V_2}\left(\frac{\partial U}{\partial V}\right)_T dV$$

ideal gas

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

but

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

*monatomic:* $E = \frac{3}{2}nRT$ *doesn't depend on V (kinetic energy only T)*

$$dU = n\bar{C}_V\,dT$$
$$\Delta U = n\bar{C}_V\,\Delta T$$

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
$$\Delta U = n\bar{C}_V\,\Delta T \quad \begin{array}{c}\Delta U = nada\\ no\,effect\,on\,U\end{array}$$

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$$n\bar{C}_P \equiv \left(\frac{dq}{dT}\right)_P \quad \boldsymbol{C_P \text{ vs } C_V}\ (E\&R_{4th}\,p.76) \quad n\bar{C}_V \equiv \left(\frac{dq}{dT}\right)_V$$

**In general**

for only P-V work and closed system ($dw_{other} = 0$, dn=0)
$$dU = dq - P_{ext}dV \quad \text{for infinitesimal change } P_{ext} = P_{int} = P$$
$$dq = dU + PdV$$

*divide by dT, V const* $\quad n\bar{C}_V = \left(\frac{dq}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V + P\left(\frac{\partial V}{\partial T}\right)_V^{=0} = \left(\frac{\partial U}{\partial T}\right)_V = n\bar{C}_V$

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

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

*now to get* $\left(\frac{\partial U}{\partial T}\right)_P$:
*in terms of T,V*

*divide by dT, P const* $\quad \left(\frac{\partial U}{\partial T}\right)_P = n\bar{C}_V\left(\frac{\partial T}{\partial T}\right)_P^{=1} + \left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$

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

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

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

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

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

- energy to raise T 1° const P (vol changes)
- energy to raise T 1° const V
- potential energy as molecules 'separate' per unit volume change
- restore energy lost as P-V work per unit volume change
- volume change per T change of 1°

- 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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**$C_P$ vs $C_V$ for ideal gas**

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

for ideal gas
$$V = \frac{nRT}{P}$$
Energy, U is function of ONLY T, i.e. U=U(T)

**so:**
$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}$$
$$\left(\frac{\partial U}{\partial V}\right)_T = \boxed{0}$$

$$n\bar{C}_P = n\bar{C}_V + [0 + P]\frac{nR}{P}$$
$$n\bar{C}_P = n\bar{C}_V + nR$$
$$\boxed{\bar{C}_P = \bar{C}_V + R \quad \text{for ideal gas}}$$

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**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 | H₂ | 20.4 | 28.8 | 8.45 | 1.41 |
| Diatomic | O₂ | 21.0 | 29.3 | 8.32 | 1.40 |
| Diatomic | N₂ | 20.8 | 29.1 | 8.32 | 1.40 |
| Triatomic | H₂O | 27.0 | 35.4 | 8.35 | 1.31 |
| Polyatomic | CH₄ | 27.1 | 35.4 | 8.36 | 1.31 |

R=8.31 J mol⁻¹ K⁻¹

ideal gas
$$\bar{C}_P - \bar{C}_V = R$$
$$monatomic\ \bar{C}_V = \frac{3}{2}R$$
$$diatomic\ \bar{C}_V \cong \frac{5}{2}R$$
$$J\ mol^{-1}\ K^{-1}$$
$$\frac{3}{2}R = 12.47$$
$$\frac{5}{2}R = 20.78$$
$$\frac{7}{2}R = 29.10$$

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

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# Chemistry 163B Winter 2020
# notes for lecture 5 Math and Enthalpy

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**1st Law recapitulation**

$U \equiv$ internal energy

$dU_{sys} = \bar{d}q_{sys} + \bar{d}w_{sys} + \bar{d}n_{sys}$ (n=number of moles; dn=0 for closed system)

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

$dU$ is exact differential

$U$ is a state function $\qquad\qquad$ completely general

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

$$dU = \bar{d}q - P_{ext}dV$$

- **Constant volume process** $dU_V = \bar{d}q_V$ $\quad$ $\Delta U_V = q_V$

- **Adiabatic process** $\qquad$ $dU = \bar{d}w$ $\quad$ $\Delta U = w$

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**enthalpy: q for process at constant Pressure**

$H \equiv U + P_{int}V$ $\qquad$ (definition of enthalpy, H)

since U is state function; and since P, V
are state variables, H is also a

**STATE FUNCTION** $\qquad$ completely general

why a new state function you might ask??

$dU_V = \bar{d}q_V$ $\quad$ ; $\quad$ $\Delta U_V = q_V$ $\quad$ *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

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**enthalpy: H, a state function for heat transfer at constant pressure**

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

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

$dH = \bar{d}q - PdV + \bar{d}w_{other} + PdV + VdP$

$dH = \bar{d}q + VdP + \bar{d}w_{other}$

$\quad$ and at P=constant and $\quad$ $\bar{d}w_{other} = 0$

$dH_P = \bar{d}q_P$

$\Delta H_P = q_P$ $\quad$ as advertised !!

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

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

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

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**ΔH ideal gas**

$\Delta H_P = q_P = \int n\bar{C}_P dT \approx n\bar{C}_P \Delta T$ $\quad$ $\boxed{\bar{C}_P \text{ independent of } T}$ (general, for $w_{other} = 0$, dn = 0)

but for ideal gas

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

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

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

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

$dH = n\bar{C}_P dT$ $\quad$ IDEAL GAS ANYTIME,
$\qquad\qquad\qquad$ EVEN IF P NOT CONSTANT

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

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**manipulating thermodynamic functions: fun and games**

**GOALS:**

- Evaluate changes in thermodynamic functions
  in terms of selected constraints
  e.g. $\left(\frac{\partial V}{\partial T}\right)$

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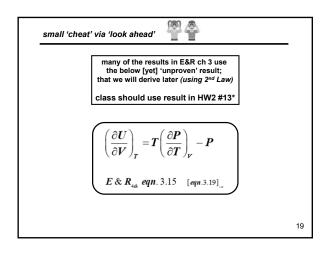  P,V,T or other directly measurable quantities.

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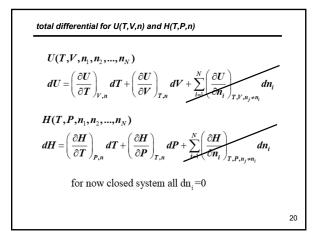---

**manipulating thermodynamic functions: fun and games**

for example:
HW#2

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

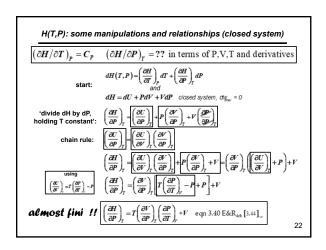$$C_V = -\left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_U$$

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**Slide 19**

*small 'cheat' via 'look ahead'*

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  [eqn. 3.19]$_{3rd}$

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**Slide 20**

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

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

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

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

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

for now closed system all $dn_i = 0$

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**Slide 21**

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

$$dU(T,V) = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad \text{closed system, } đw_{other}=0$$

$$dU(T,V) = đq - PdV$$

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

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

$$\text{hmmm}\left(\frac{đq}{dV}\right)_T \overset{??}{=} T\left(\frac{\partial P}{\partial T}\right)_V \quad \text{see you later}$$

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

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

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

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**Slide 22**

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

$(\partial H/\partial T)_P = C_P$   $(\partial H/\partial P)_T = ??$ 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

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

'divide dH by dP, holding T constant':  $\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T + V\left(\frac{\partial P}{\partial P}\right)_T$

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

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**Slide 23**

*so finishing up for dU and dH:*

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

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

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

similar to HW#1 prob 1d-e  $0 = \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_P$

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

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

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

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

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

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**Slide 24**

*in section derive equation following equation*

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

**start with**

$$dU = dH - PdV - VdP$$

**divide by $dT$ with V constant**
**and then boogie along as we just did!!**

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# Chemistry 163B Winter 2020
## notes for lecture 5 Math and Enthalpy

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### First Law: ideal gas calculations

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

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

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

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### Lecture 5: GOALS

- ✓ Some new math 'tricks'

- ✓ for *ideal gas* $\Delta U = n\ \bar{C}_V \Delta T$ 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* $\Delta H = n\ \bar{C}_P \Delta T$ along any path *(even if P changes along path)*

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

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### END OF LECTURE 5

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### why is $C_V$ larger for diatomic than for monatomic gas ?

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

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

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

translational and rotational modes

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

*activated at high T*

http://images.flatworldknowledge.com/averillfwk/averillfwk-fig18_013.jpg



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) |

https://www.slideserve.com/marlee/chapter-2-the-first-law-the-concepts

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