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

Chemistry 163B

Lecture 5 Winter 2020

Mathematics for Thermodynamics
Enthalpy

Challenged Penmanship Notes

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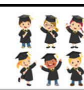
Lecture 5: GOALS



- 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 *(math handout item #3; E&R ch. 3)*

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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differential of product (product rule)

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

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example of implication of total differentials

First Law

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

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

for $dn = 0$ (closed system)

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

OR

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

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"divide through by ??"

math handout item #6

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

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

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

- for any substance

$dU_V = đq_V = n\bar{C}_V\, dT$ and $\Delta U_V = \int n\bar{C}_V\, dT$ 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 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)

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

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

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

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

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

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

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

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

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

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

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

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

In general

for only P-V work and closed system ($\text{đ}w_{other}=0$, dn=0)

$dU = \text{đ}q - P_{ext}dV$ *for infintesimal change $P_{ext} = P_{int} = P$*

$$\text{đ}q = dU + PdV$$

divide by dT, V const $\quad n\bar{C}_V \equiv \left(\frac{\text{đ}q}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V + P\underbrace{\left(\frac{\partial V}{\partial T}\right)_V}_{=0} = \left(\frac{\partial U}{\partial T}\right)_V = n\bar{C}_V$

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

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

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

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

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

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

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

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

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

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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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:

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

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

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

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

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

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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	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_2O	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

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

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

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

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

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

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

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

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

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1st Law recapitulation

U ≡ internal energy

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

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

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** $dU_V = đq_V$ $\quad \Delta U_V = q_V$
- **Adiabatic process** $dU = đw$ $\quad \Delta U = w$

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enthalpy: q for process at constant Pressure

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

$$dU_V = đq_V \quad ; \quad \Delta U_V = q_V \quad \textbf{heat at constant volume}$$

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

desire state function for $\mathbf{q_P}$, heat at constant pressure

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

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

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

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

$$dH = đq + \cancel{V}dP + \cancel{đw}_{other}$$

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

$$dH_P = đq_P$$

$$\Delta H_P = q_P$$ **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)

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ΔH ideal gas

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

but for ideal gas

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

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

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

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

$$dH = n\bar{C}_P dT$$ IDEAL GAS ANYTIME, 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. $\left(\frac{\partial V}{\partial T}\right)_P$
- 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.

GENERAL GENERAL GENERAL

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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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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*

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

$\boldsymbol{E}$ & $\boldsymbol{R}_{4th}$ ***eqn.*** 3.15 [***eqn***.3.19]$_{3rd}$

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

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

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

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

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

for now closed system all $dn_i = 0$

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

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

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

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

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

hmmm $\left(\frac{\bar{d}q}{dV}\right)_T \stackrel{??}{=} T\left(\frac{\partial P}{\partial T}\right)_V$ 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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H(T,P): some manipulations and relationships (closed system)

$(\partial H/\partial T)_P = C_P \qquad (\partial H/\partial P)_T = ??$ 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, $\bar{d}w_{other} = 0$

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

chain rule: $$\boxed{\left(\frac{\partial U}{\partial P}\right)_T} = \boxed{\left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial P}\right)_T}$$

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

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

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

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

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so finishing up for dU and dH:

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

similar to HW#1 prob 1d-e

$$V(T,P)\quad dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \left(\frac{\partial V}{\partial T}\right)_V$$
$$= \left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial T}{\partial T}\right)_V + \left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_V$$
$$0 = \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_V$$
$$\boxed{\left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_V} = \boxed{-\left(\frac{\partial V}{\partial T}\right)_P}$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\boxed{\left(\frac{\partial V}{\partial T}\right)_P}$$ 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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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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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**):

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

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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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END OF LECTURE 5

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why is C_V larger for diatomic than for monatomic gas ?

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

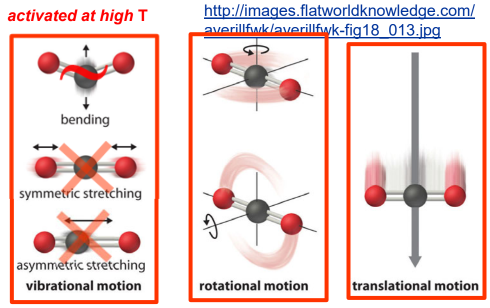
$$\text{diatomic } \bar{C}_V \cong \frac{5}{2}R$$

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

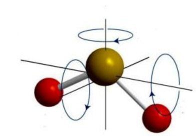
translational and rotational modes each contribute $\frac{1}{2}$ R to $\bar{C}_V$

activated at high T

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



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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