Chemistry 163B

Lecture 5 Winter 2014
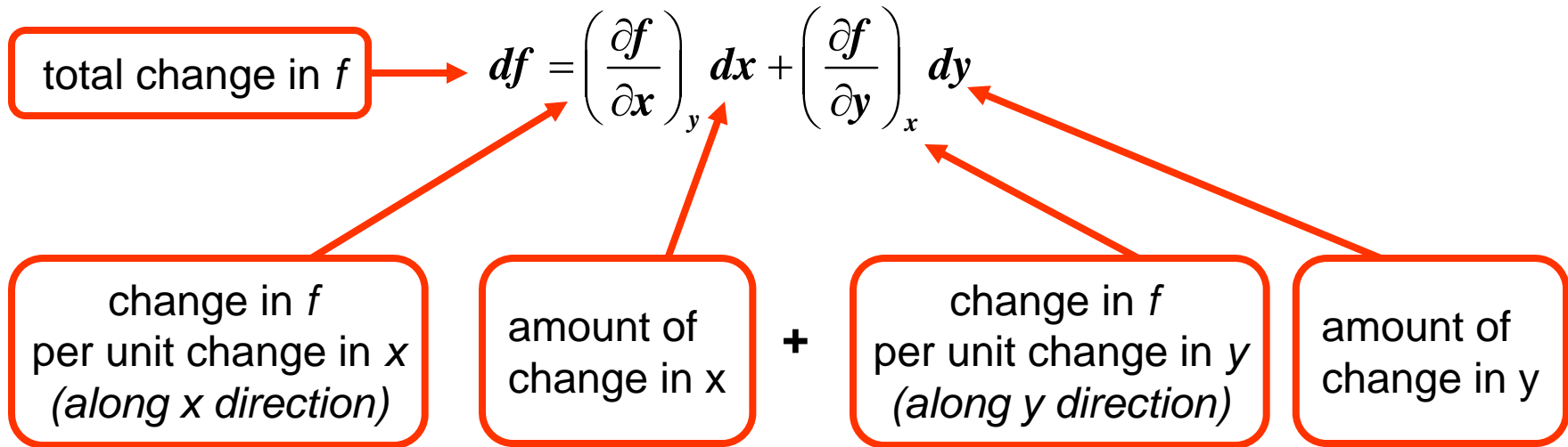
Challenged Penmanship

Notes

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

$$f(x,y) \quad \text{a well behaved function}$$

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

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

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

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

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

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

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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math handout #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

two relationships for ideal gasses: a (μsec) look ahead
(will prove rigorously in next lecture, but gthis is the next lecture)

- for any substance

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

- but for an ideal gas

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

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

- for ideal gas

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

- monatomic ideal gas

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

[simple proof coming soon]

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

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

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

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

$$dU = \bar{d}q - PdV$$

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

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

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

ideal gas

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

but

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

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

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

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

ΔU along general path where both T (const V) and V (const T) vary

$$\Delta U = n\bar{C}_V\,\Delta T \qquad\qquad nada$$

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$C_P = C_V + nR$ for ideal gas

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

$$dU = đq - P_{ext}dV$$

$$dU_V = đq_V = n\overline{C_V}\,dT \qquad dU_p = đq_p - PdV_P$$

$$đq_p = dU_p + PdV_P$$

$$\left(\frac{đq}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V = n\overline{C_V} \qquad \left(\frac{đq}{dT}\right)_P = n\overline{C_P} = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

for monatomic ideal gas

$$PV = nRT \text{ and } U = \frac{3}{2}nRT$$

$$\left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}nR = \left(\frac{\partial U}{\partial T}\right)_P$$

$$n\overline{C_P} = \frac{3}{2}nR + P\left(\frac{nR}{P}\right) = \frac{5}{2}nR$$

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1st Law recapitulation

$U \equiv$ internal energy

$dU_{sys} = đq_{sys} + đw_{sys} + dn_{sys}$ (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)

$$dU = đq - P_{ext}dV$$

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

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

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

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

STATE FUNCTION *completely general*

why a new state function you might ask??

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

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

desire state function for **q$_P$**, heat at constant pressure

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

$$dH = dU + PdV + VdP$$

$$dH = \text{đ}q - PdV + \text{đ}w_{other} + PdV + VdP$$

$$dH = \text{đ}q + VdP + \text{đ}w_{other}$$

and at P=constant and $\text{đ}w_{other} = 0$

$$dH_P = \text{đ}q_P$$

$$\Delta H_P = q_P \quad \text{as advertised !!}$$

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

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

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

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

ideal gas

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

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

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

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

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

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

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

for example:
HW#3

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

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

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

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

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

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

for now closed system all $dn_i = 0$

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

$$dH = đq + VdP \quad \text{closed system, } đw_{other} = 0$$

'divide by dT, holding P constant'

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

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

'divide by dP, holding T constant'

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

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

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

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

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$$dU = đq - PdV \quad \text{closed system,} \ đw_{other} = 0$$

'divide by dT, holding V constant'

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

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

'divide by dV, holding T constant'

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

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

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

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

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

need 2nd 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*

$$\frac{1}{n}\left(\frac{\partial H}{\partial T}\right)_P = \bar{C}_P \quad and \quad \frac{1}{n}\left(\frac{\partial U}{\partial T}\right)_V = \bar{C}_V$$

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

$$H = U + PV$$

$$dH = dU + PdV + VdP$$

$$H = U + PV$$

$$dH = dU + PdV + VdP$$

divide by dT, P constant

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

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

now to get $\left(\dfrac{\partial U}{\partial T}\right)_P$

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

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

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

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

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

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

volume change per T change of 1⁰

energy to raise T 1⁰ const P (vol changes)

energy to raise T 1⁰ const V

potential energy as molecules 'separate' per unit volume change

energy lost as P-V work per unit volume change

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

for ideal gas

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

Energy, U is function of ONLY T, U(T)

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

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

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

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

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

experimental C_V and C_P for selected gasses

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

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

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

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

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

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

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

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

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

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

start with

$$dU = dH - PdV - VdP$$

divide by dT with V constant

and then boogie along as we just did!!

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