Chemistry 163B Winter 2014
notes for lecture 5

Chemistry 163B

Lecture 5 Winter 2014

Challenged Penmanship

Notes

1

total differential *(math handout #4; E&R ch. 3)*

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

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

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

- total change in *f* → df
- change in *f* per unit change in *x* *(along x direction)* → $\left(\frac{\partial f}{\partial x}\right)_y$
- amount of change in x → dx
- \+
- change in *f* per unit change in *y* *(along y direction)* → $\left(\frac{\partial f}{\partial y}\right)_x$
- amount of change in y → dy

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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

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

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

⬇

$dn = 0$ (closed system)

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

OR

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

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"divide through by ??"

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

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

- for any substance

  $dU_V = đq_V = n\bar{C}_V\, dT$ **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

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

  [simple proof coming soon]

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

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

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

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

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$C_P = C_V + nR$ for ideal gas

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

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

$$dU_V = \bar{d}q_V = n\bar{C}_V\, dT$$

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

$$dU_p = \bar{d}q_p - PdV_P$$

$$\bar{d}q_p = dU_p + PdV_P$$

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

for monatomic ideal gas

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

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

$$n\bar{C}_P = \frac{3}{2}nR + P\left(\frac{nR}{P}\right) = \frac{5}{2}nR$$

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1st Law recapitulation

U ≡ internal energy

$dU_{sys} = \bar{d}q_{sys} + \bar{d}w_{sys} + dn_{sys}$ (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)

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

- **Constant volume process** $dU_V = \bar{d}q_V$ $\Delta U_V = q_V$
- **Adiabatic process** $dU = \bar{d}w$ $\Delta U = w$

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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 P, V are state variables, H is also a

STATE FUNCTION *completely general*

why a new state function you might ask??

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

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

desire state function for q_P, heat at constant pressure

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

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

$$dH = dU + PdV + VdP$$

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

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

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

$$dH_P = \bar{d}q_P$$

$\Delta H_P = q_P$ 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)

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ΔH ideal gas

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

ideal gas

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

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

$dH = n\bar{C}_V dT + nRdT$ (general for idel 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

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

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manipulating thermodynamic functions: fun and games

for example:
HW#3

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

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

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

$$U(T,V,n_1,n_2,\ldots,n_N)$$

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

$$H(T,P,n_1,n_2,\ldots,n_N)$$

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

for now closed system all $dn_i=0$

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

$$dH = \text{đ}q + VdP \quad \text{closed system, } \text{đ}w_{other}=0$$

math handout #6

'divide by dT, holding P constant'

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

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

'divide by dP, holding T constant'

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

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

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

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

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

$$dU = \text{đ}q - PdV \quad \text{closed system, } \text{đ}w_{other}=0$$

'divide by dT, holding V constant'

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

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

'divide by dV, holding T constant'

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

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

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

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

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save for later when we have tools from 2nd Law of Thermodynamics

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

need 2nd Law to evaluate this in terms of P,V,T

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \qquad E\,\&\,R \quad eqn.3.19$$

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*

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some important relationships between C_P and C_V

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

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

$$H = U + PV$$

$$dH = dU + PdV + VdP$$

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continuing with relating C_P and C_V

$$H = U + PV$$
$$dH = dU + PdV + VdP$$

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 $\left(\frac{\partial U}{\partial T}\right)_P$

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

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

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

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

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

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

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

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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, U(T)

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

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

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

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

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

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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

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

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

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

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

$$\frac{3}{2}R = 12.47$$
$$\frac{5}{2}R = 20.78$$
$$\frac{7}{2}R = 29.10$$

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

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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):

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

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