Chemistry 163B Winter 2013
notes for lecture 4

Chemistry 163B

Lecture 4 Winter 2013

Challenged Penmanship

Notes

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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** $dU = đw$ $\Delta U = w$

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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??

$dU_V = đq_V$; $\Delta U_V = q_V$ *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

$$H \equiv U + P_{in}V$$
$$dH = dU + PdV + VdP$$
$$dH = đq - PdV + đw_{other} + PdV + VdP$$
$$dH = đq + VdP + đw_{other}$$

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 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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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**

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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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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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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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'   math handout #6

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

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

'divide by dP, holding T constant'

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

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

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

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

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

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

'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'

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

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

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

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

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

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

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

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

many of the results in E&R ch 3 use this [yet] 'unproven' result; we will derive later class should use result in HW2 #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

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

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

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

- 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
- energy lost as P-V work per unit volume change
- volume change per T change of 1°

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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)

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

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

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

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

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

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experimental C_V and C_P for selected gasses

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

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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