Chemistry 163B

Lecture 4 Winter 2013

Challenged Penmanship

Notes

1st Law recapitulation

$U \equiv$ internal energy

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

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

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

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??

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

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

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

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

$$dH = dU + PdV + VdP$$

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

$$dH = đq + VdP + đw_{other}$$

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

$$dH_P = đq_P$$

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

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

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

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

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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for example:
HW#2

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

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

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

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

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

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

for now closed system all $dn_i = 0$

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

'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'

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

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

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

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

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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'

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

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

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

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

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

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

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

**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***

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

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

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

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

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

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

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

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

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

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

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

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

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)

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

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

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

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

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

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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

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

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

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

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

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

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

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

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!!