Chemistry 163B

Lectures 6-7
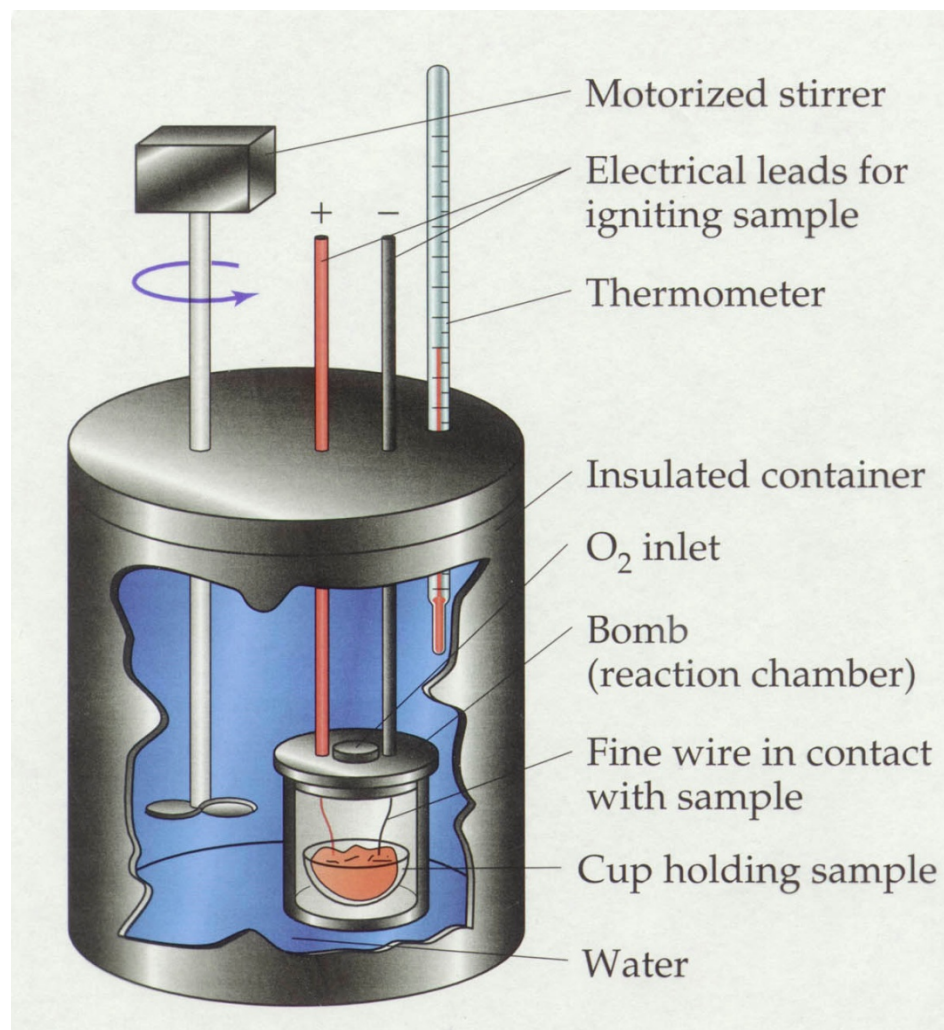
Thermochemistry

Chapter 4 Engel & Reid

$$\Delta U_V = q_V$$

$$\Delta U = U_{products} - U_{reactants}$$

Motorized stirrer

Electrical leads for igniting sample

Thermometer

Insulated container

O_2 inlet

Bomb (reaction chamber)

Fine wire in contact with sample

Cup holding sample

Water

$$\Delta U_V = q_V$$

$$\Delta U = U_{products} - U_{reactants}$$

Stirrer

Ignition wires

Thermometer

Diathermal container

Steel bomb

Reactants in sample cup
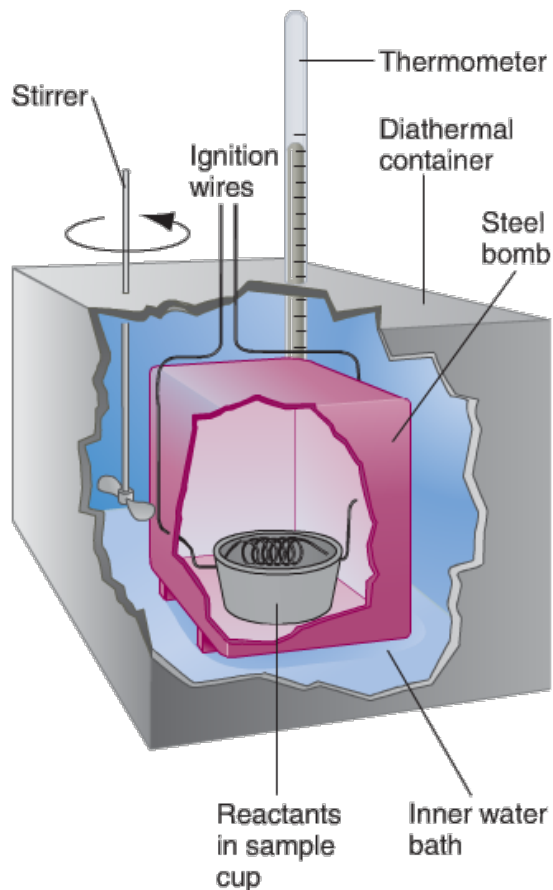
Inner water bath

FIGURE 4.3

FIGURE 4.3
Schematic diagram of a bomb calorimeter. The liquid or solid reactant is placed in a cup suspended in the thick-walled steel bomb, which is filled with O_2 gas. The vessel is immersed in an inner water bath, and its temperature is monitored. The diathermal container is immersed in an outer water bath (not shown) whose temperature is maintained at the same value as the inner bath through a heating coil. By doing so, there is no heat exchange between the inner water bath and the rest of the universe.
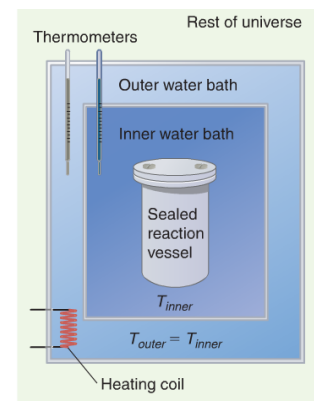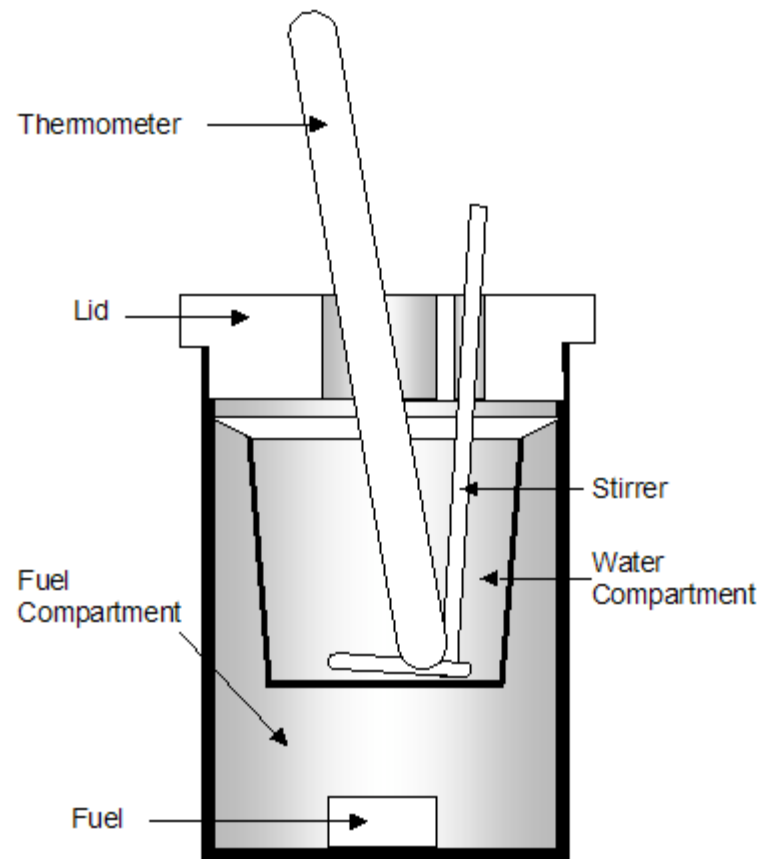
Rest of universe

Thermometers

Outer water bath

Inner water bath

Sealed reaction vessel

T_{inner}

$T_{outer} = T_{inner}$

Heating coil

FIGURE 2.3
An isolated composite system is created in which the surroundings to the system of interest are limited in extent. The walls surrounding the inner water bath are rigid.

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$$\Delta H_P = q_P$$

$$\Delta H = H_{products} - H_{reactants}$$

Thermometer

Lid

Fuel Compartment

Fuel

Stirrer

Water Compartment

$$\Delta H_P = q_P$$
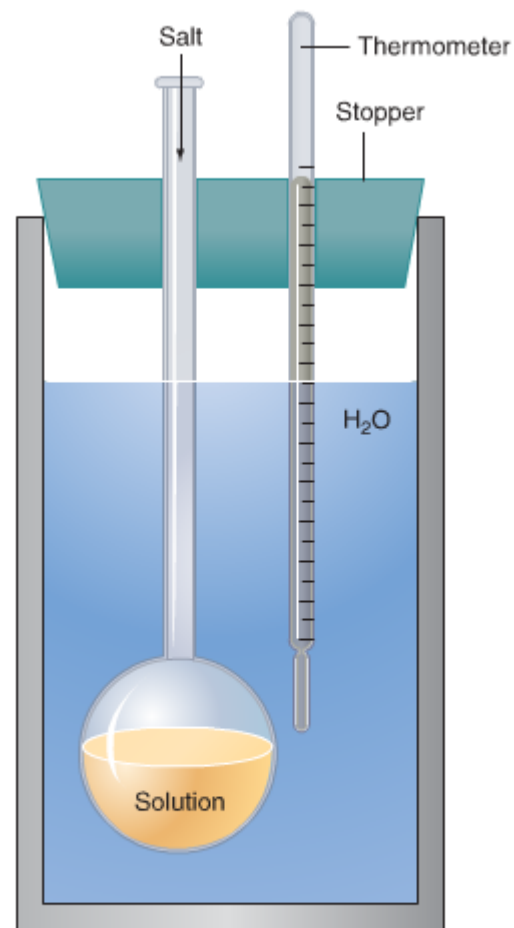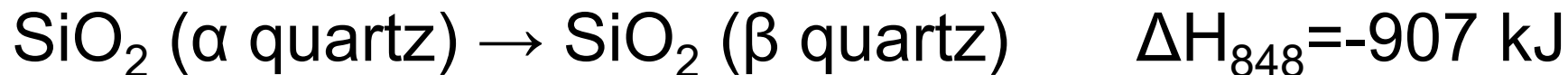
$$\Delta H = H_{products} - H_{reactants}$$

FIGURE 4.4
Schematic diagram of a constant pressure calorimeter suitable for measuring the enthalpy of solution of a salt in water.

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$$C(gr) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H_{298} = -393 \text{ kJ}$$

$$ATP + H_2O \rightarrow ADP + H_3PO_4 \qquad \Delta H_{298} \approx -20.5 \text{ kJ}$$

$$SiO_2 (\alpha \text{ quartz}) \rightarrow SiO_2 (\beta \text{ quartz}) \qquad \Delta H_{848} = -907 \text{ kJ}$$

$$NaCl(s) + H_2O (\ell) \rightarrow Na^+(aq) + Cl^-(aq) \quad \Delta H_{298} = +3.9 \text{ kJ}$$
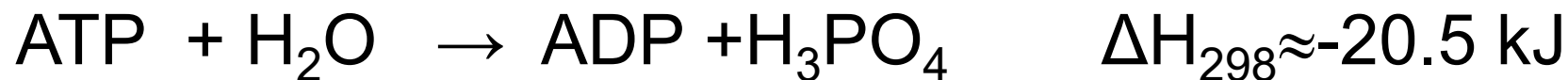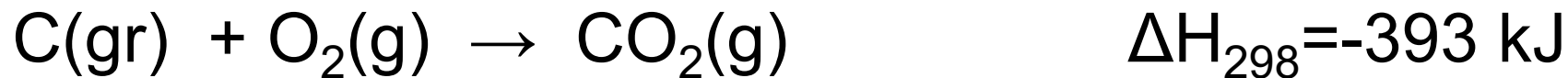
HW#3 16,17,18   • Calculate $\Delta H_{reaction}$
Hess's Law, standard heats of formation

HW#3 16,21   • $\Delta H_{reaction}$ vs $\Delta U_{reaction}$

HW#3 18, *19   • Temperature (*and later* pressure) dependence of $\Delta H_{reaction}$

• Calorimetry

• Heats of solution

HW#3 20   • $\Delta H_{reaction}$ from bond enthalpies

$$\Delta H_{reaction} = H_{products} - H_{reactants}$$

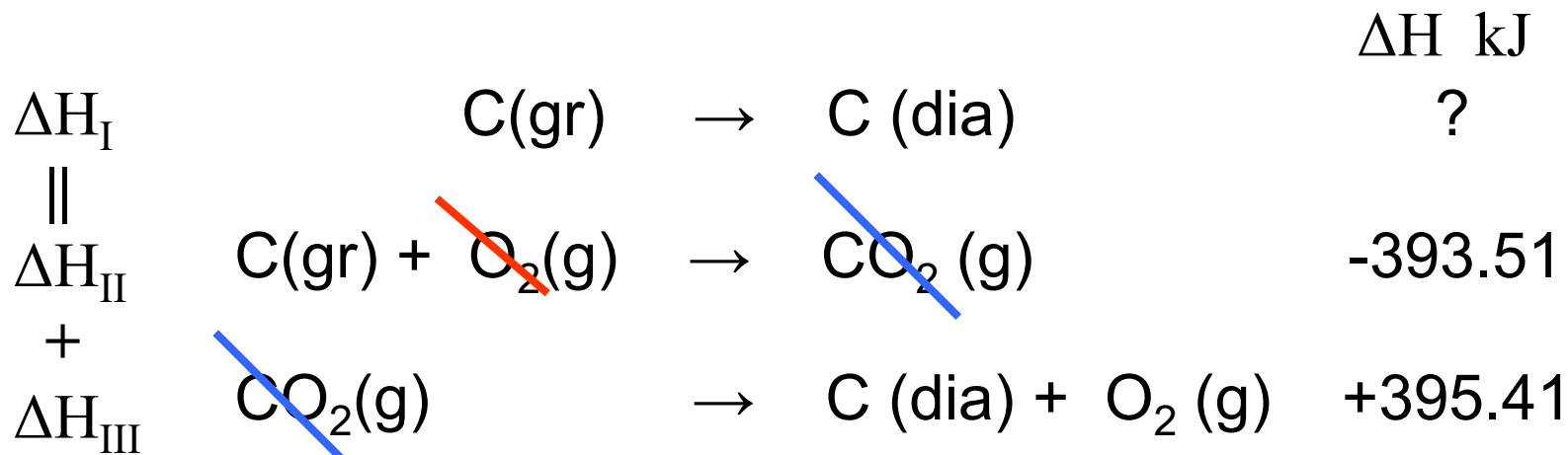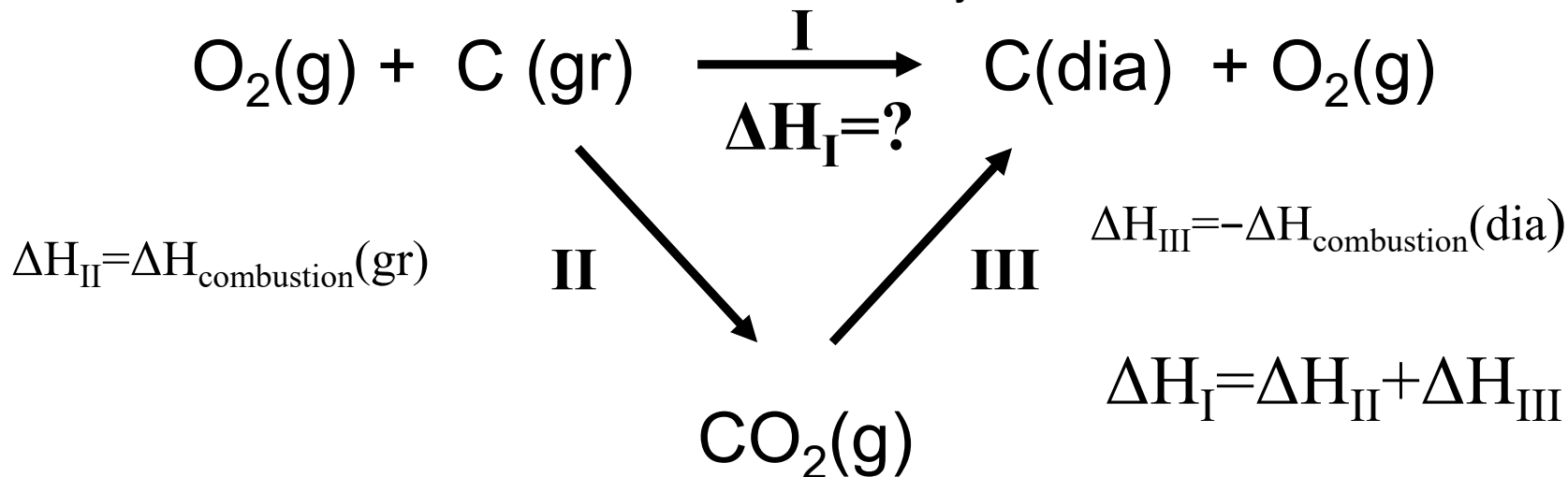## ΔH State Function ⇨ Hess's Law

can't measure directly

$$O_2(g) + C(gr) \xrightarrow[\Delta H_I=?]{I} C(dia) + O_2(g)$$

$\Delta H_{II} = \Delta H_{combustion}(gr)$ **II**   **III** $\Delta H_{III} = -\Delta H_{combustion}(dia)$

$$CO_2(g)$$

$$\Delta H_I = \Delta H_{II} + \Delta H_{III}$$

			ΔH kJ
ΔH_I	$C(gr)$	$\rightarrow$ $C(dia)$	?
$\parallel$			
ΔH_{II}	$C(gr) + O_2(g)$	$\rightarrow$ $CO_2(g)$	-393.51
+			
ΔH_{III}	$CO_2(g)$	$\rightarrow$ $C(dia) + O_2(g)$	+395.41

$$\Delta H_I = \Delta H_{II} + \Delta H_{III} = 1.90 \text{ kJ}$$

- ## stoichiometry
  ΔH *is extensive*; $\Delta \bar{H}$ *is intensive*

- ## physical state
  phase or crystal form of reactants and products

- ## temperature and pressure

- ## does **NOT** depend on path

$$n_A A + n_B B \rightarrow n_C C + n_D D \qquad \Delta H_{reaction} = n_C \bar{H}_C + n_D \bar{H}_D - n_A \bar{H}_A - n_B \bar{H}_B$$

total enthalpy of reactants

molar enthalpy of reactant i

number of moles of i in stoichiometry

$$H_{prods} = \sum_{i=prods} n_i \bar{H}_i \qquad H_{reacts} = \sum_{i=reacts} n_i \bar{H}_i$$

$$\Delta H_{reaction} = \sum_{i=prods} n_i \bar{H}_i - \sum_{i=reacts} n_i \bar{H}_i$$

ν_i *is stoichiometric coefficient of ith reactant / product*

$$\nu_i = n_i \text{ if } i \text{ is product species}$$

$$\nu_i = -n_i \text{ if } i \text{ is reactant species}$$

$$\boxed{\Delta H_{reaction} = \sum_i \nu_i \bar{H}_i}$$

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$\Delta H_{reaction}$ vs $\Delta U_{reaction}$ at fixed temperature T

$$H \equiv U + PV$$

$$\Delta H = H_{prods} - H_{reacts}$$

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + (PV)_{prods} - (PV)_{reacts}$$

assume:
 i) PV and ΔPV is small for solids and liquids
 ii) Gasses follow ideal gas law
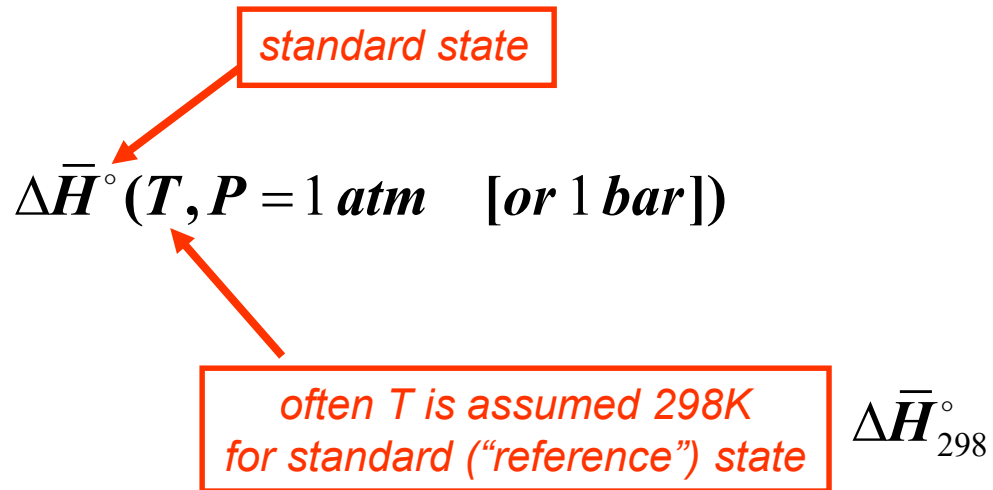
$$\Delta PV = (PV)_{prods} - (PV)_{reacts}$$

$$\Delta PV = (n_{gas}RT)_{prod} - (n_{gas}RT)_{react}$$

$$\Delta PV = \Delta n_{gas}RT$$

$$\Delta H_{reaction} = \Delta U_{reaction} + \Delta n_{gas}RT$$

E&R$_{4th}$ eqn 4.23 ??

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standard states and enthalpies of formation (0, 1mol $\equiv \theta$ $_{E\&R}$)

standard state

$$\Delta \bar{H}^{\circ}(T, P = 1\,atm \quad [or\,1\,bar])$$

often T is assumed 298K
for standard ("reference") state

$$\Delta \bar{H}^{\circ}_{298}$$
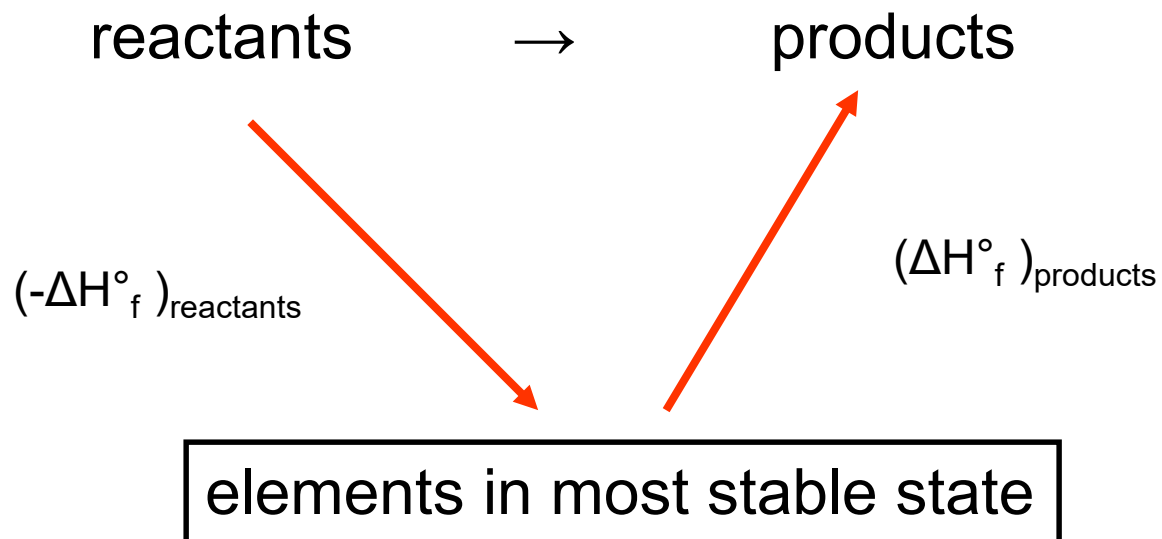
define standard states →

$$(\Delta \bar{H}^{\circ}_{298})_{formation} \equiv \bar{H}^{\circ}_{f}$$

molar enthalpy
of formation

define enthalpy of formation →

reactants $\rightarrow$ products

$(-\Delta H°_f)_{reactants}$

$(\Delta H°_f)_{products}$

elements in most stable state

$$(\Delta H°)_{rxn} = \sum_i \upsilon_i (\bar{H}^0_f)_i$$

do HW#3 problem 16b (E&R P4.33b)
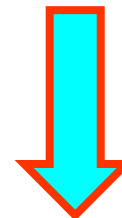
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✔ • Calculate $\Delta H_{reaction}$
Hess's Law, standard heats of formation

✔ • $\Delta H_{reaction}$ vs $\Delta U_{reaction}$

• Temperature (and pressure) dependence of $\Delta H_{reaction}$

• Calorimetry

• Heats of solution

• $\Delta H_{reaction}$ from bond enthalpies

- - - - - - - - - - - - - - - - - **MIDTERM 1** - - - - - - - - - - - - -

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

for a given reactant or product at constant P

$$dH_P = n\bar{C}_P dT \qquad d\bar{H}_P = \bar{C}_P dT$$

$$\int_{T_1}^{T_2} d\bar{H} = \int_{T_1}^{T_2} \bar{C}_P dT$$

change in enthalpy of substance $T_1 \rightarrow T_2$

$$\bar{H}(T_2) - \bar{H}(T_1) = \int_{T_1}^{T_2} \bar{C}_P dT$$

$$\bar{H}(T_2) = \bar{H}(T_1) + \int_{T_1}^{T_2} \bar{C}_P dT$$

$$\Delta H_{reaction} = \sum_i v_i \bar{H}_i \qquad \left(\Delta C_P\right)_{reaction} = \sum_i v_i \left(\bar{C}_P\right)_i$$

$$\Delta H_{rxn}\left(T_1, P\right)$$

vs

$$\bar{H}_i(T_2) = \bar{H}_i(T_1) + \int_{T_1}^{T_2} (\bar{C}_P)_i dT$$

$$\Delta H_{rxn}\left(T_2, P\right)$$

$$\Delta H_{reaction}(T_2) = \sum_j v_i \bar{H}_i(T_2)$$

$$\sum_j v_i \bar{H}_i(T_2) = \sum_j v_i \bar{H}_i(T_1) + \sum_i v_i \int_{T_1}^{T_2} (\bar{C}_P)_i dT$$

$$\Delta H_{reaction}(T_2) = \Delta H_{reaction}(T_1) + \int_{T_1}^{T_2} \sum_i v_i (\bar{C}_P)_i dT$$

change of ΔH_{rxn}
$T_1 \rightarrow T_2$

$$\Delta H_{reaction}(T_2) = \Delta H_{reaction}(T_1) + \int_{T_1}^{T_2} \Delta C_P dT$$

$$where \quad \Delta C_P = \sum_i v_i (\bar{C}_P)_i = "(C_P)_{products} - (C_P)_{reactants}"$$

$$3C_2H_2 \text{ (g)} \rightarrow C_6H_6 \text{ (ℓ)} \quad \text{calc } \Delta H^{\circ}_{298}$$

$\left(\Delta \bar{H}^{\circ}_f\right)_{298^{\circ}}$ 227.4   49.1 $kJ\ mol^{-1}$

$\left(\Delta H^{\circ}\right)_{298^{\circ}}$ $-3(227.4) + 1(49.1) = -633.1\ kJ$ $[per\ mol\ C_6H_6\ (\ell)]$

(mol) (kJ mol^{-1}) + (mol)(kJ mol^{-1}) = kJ

$$3C_2H_2 \text{ (g)} \rightarrow C_6H_6 \text{ (ℓ)} \quad \text{calc } \Delta H^{\circ}_{398}$$

$\bar{C}_P$ 44.   136.0 $(J\ K^{-1}\ mol^{-1})$

$\Delta \bar{C}_P$ $\text{-}3(44.0) + 1(136.0) = 4.0\ (J\ K^{-1})$

$$\left(\Delta H^{\circ}\right)_{398^{\circ}} = \left(\Delta H^{\circ}\right)_{298^{\circ}} + \int_{298}^{398} \Delta C_P dT = \left(\Delta H^{\circ}\right)_{298^{\circ}} + \Delta C_P\ \Delta T$$

C_P independent of T

$$\left(\Delta H^{\circ}\right)_{398^{\circ}} = -633.1\ kJ + (4.0 \times 10^{-3}\ kJ\ K^{-1})(100K) = -632.7\ kJ$$

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✔ • Calculate $\Delta H_{reaction}$
   Hess's Law, standard heats of formation

✔ • $\Delta H_{reaction}$ vs $\Delta U_{reaction}$

✔ • Temperature (and pressure) dependence
   of $\Delta H_{reaction}$

• Calorimetry

• Heats of solution

• $\Delta H_{reaction}$ from bond enthalpies

MIDTERM 1

$$\Delta U_V = q_V$$

$$\Delta U = U_{products} - U_{reactants}$$

Motorized stirrer

Electrical leads for igniting sample

Thermometer

Insulated container

O_2 inlet

Bomb (reaction chamber)

Fine wire in contact with sample

Cup holding sample

Water

20

heats of reactions (constant pressure)

$$\Delta H_P = q_P$$

$$\Delta H = H_{products} - H_{reactants}$$

Thermometer

Lid

Fuel Compartment

Stirrer

Water Compartment

Fuel
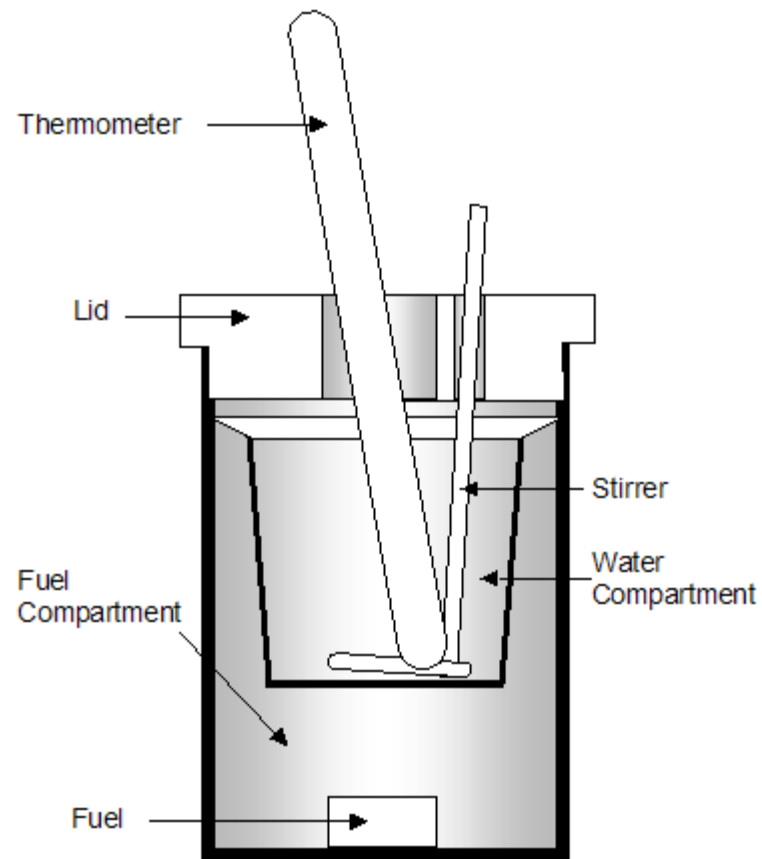
useful for small samples (often biological)
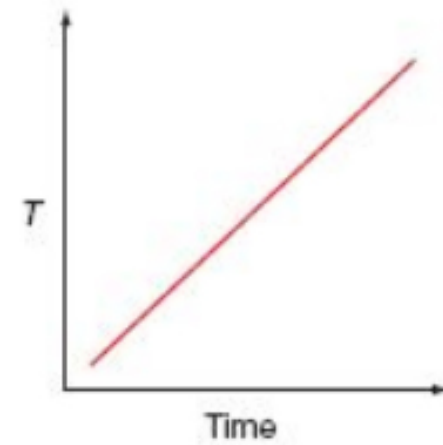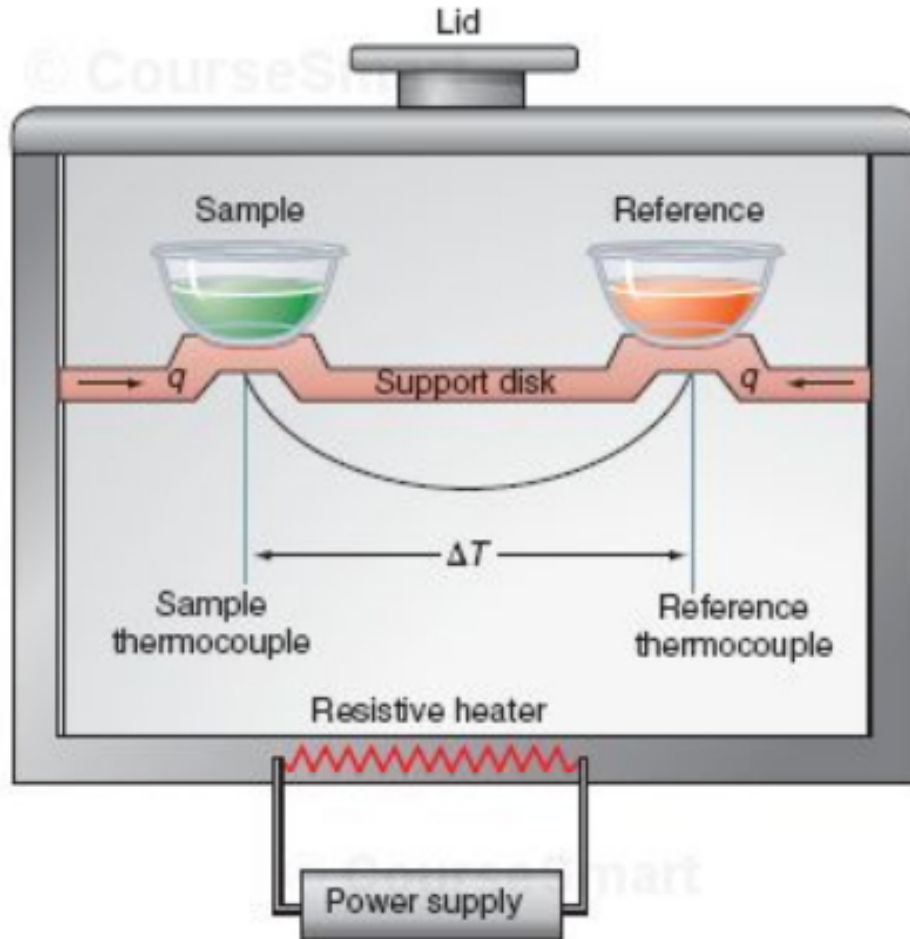
T of reference rises linearly with time

heat input

T rise due to q from calorimeter into sample
PLUS
ΔH from process (e.g. chemical reaction, phase change or protein denaturation)
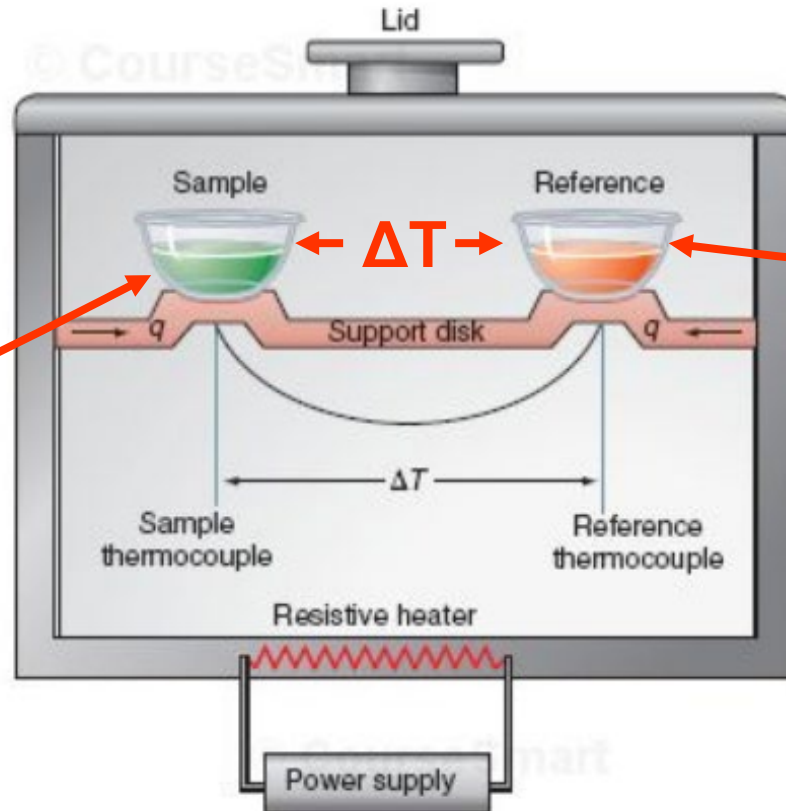
T rise due to q from calorimeter into reference

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denaturation of protein

Intermediates during denaturation
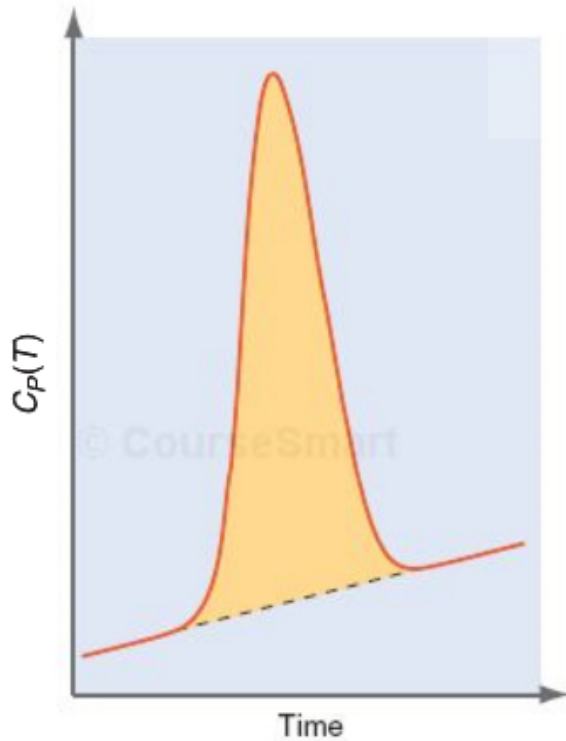
$C_{psample}$ increases during denaturation since some of q_{in} goes to denaturation

FIGURE 4.8

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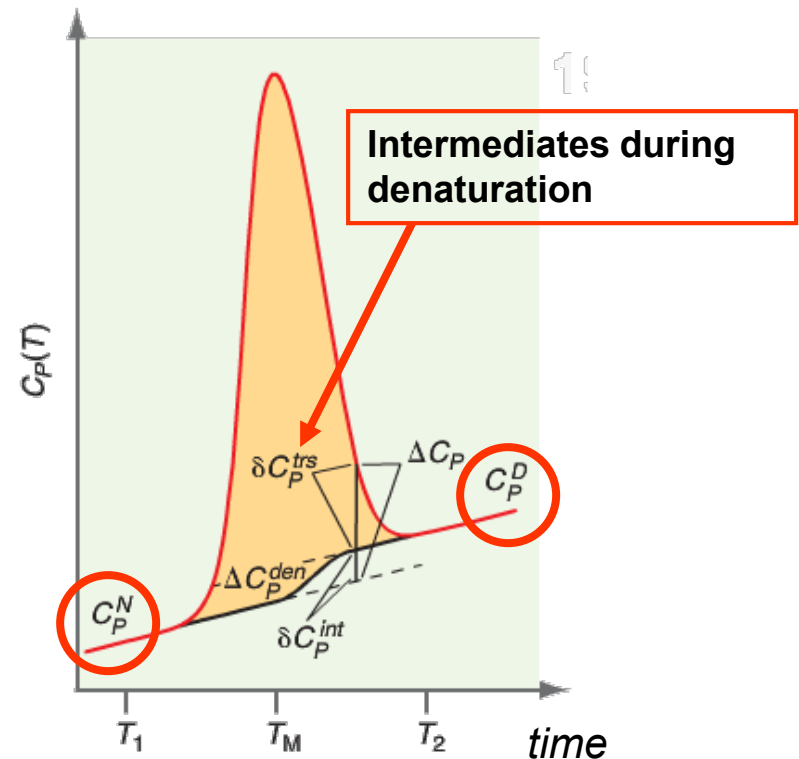
will prove later:

$$\left(\frac{\partial \bar{H}}{\partial P}\right)_{T} = \bar{V} - T\left(\frac{\partial \bar{V}}{\partial T}\right)_{P} = \bar{V} - T\bar{V}\alpha$$

$$\alpha \equiv \frac{1}{\bar{V}}\left(\frac{\partial \bar{V}}{\partial T}\right)_{P} \quad \text{the coefficient of thermal expandion}$$

$$\left(\frac{\partial \Delta H_{reaction}}{\partial P}\right)_{T} = \sum_{i} \nu_{i}(\bar{V}_{i} - T\bar{V}_{i}\alpha_{i})$$

Will show later:

dependence of $\Delta H_{reaction}$ on pressure is usually weak

<u>importance</u>: how to assign $\overline{H}_f^0$ for an individual ion in solution since ions come in 'pairs'

<u>resolution:</u> assign $\overline{H}_f^0$ (H$^+$ (aq, 1M)$_{ideal}$)=0

and measure $\overline{H}_f^0$ for other ions relative to H$^+$

another importance: HW3 #21 E&R$_{4th}$ P4.5d

21. P4.5 Calculate Δr H^o and ΔrU^o at 298.15 K for the following reactions:
d. 2NaOH(aq)+H$_2$SO$_4$(aq)→Na$_2$SO$_4$(aq)+2H$_2$O(l)

Assume complete dissociation of NaOH, H$_2$SO$_4$, and Na$_2$SO$_4$.

$$\Delta H_{reaction} = -2\Delta\overline{H}_f^0(Na^+) - 2\Delta\overline{H}_f^0(OH^-) - 2\Delta\overline{H}_f^0(H^+) - \Delta\overline{H}_f^0(SO_4^{2-})$$

$$+ 2\Delta\overline{H}_f^0(Na^+) + \Delta\overline{H}_f^0(SO_4^{2-}) + 2\Delta\overline{H}_f^0(H_2O)$$

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$$HOW\ TO\ GET\ \Delta\bar{H}^0_f\ for\ Cl^-\ (aq)$$

$$HCl(g, 1\ bar) \xrightarrow{\ H_2O\ } H^+(aq,\ 1M)_{ideal} + Cl^-(aq,\ 1M)_{ideal}$$
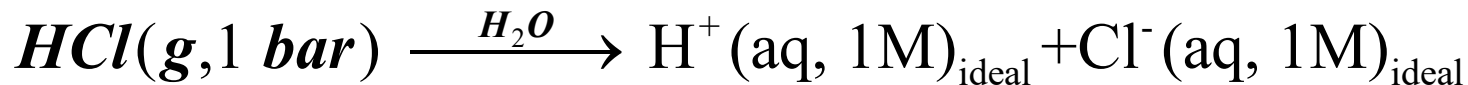
$$\Delta H_{measured} = -74.9\ kJ$$

$$-74.9\ kJ = -\Delta\bar{H}^0_f(HCl(g)) + \Delta\bar{H}^0_f(H^+(aq)) + \Delta\bar{H}^0_f(Cl^-(aq))$$

$$-74.9\ kJ = -(-92.3kJ) + 0 + \bar{H}^0_f(Cl^-(aq))$$

$$\Delta\bar{H}^0_f(Cl^-(aq)) = -167.2\ kJ\ mol^{-1}$$

$$GOT\ \Delta\bar{H}^0_f\ for\ Cl^-(aq)$$

$$NOW$$

$$\boldsymbol{GET} \; \Delta\overline{H}^0_f \; \text{for Na}^+(\boldsymbol{aq})$$

$$NaCl(s) \xrightarrow{\; H_2O \;} \text{Na}^+(\text{aq, 1M})_{\text{ideal}} + \text{Cl}^-(\text{aq, 1M})_{\text{ideal}}$$
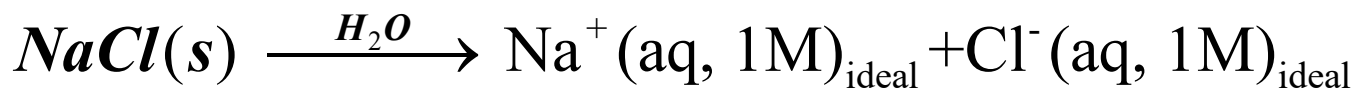
$$\Delta H_{\text{measured}} = \; +3.89 \; \text{kJ}$$

$$+3.89\text{kJ} \; = \; -\Delta\overline{H}^0_f(\text{NaCl(s)}) + \Delta\overline{H}^0_f(\text{Na}^+(\text{aq})) + \Delta\overline{H}^0_f(\text{Cl}^-(\text{aq}))$$

$$+3.89\text{kJ} \; = \; -(-411.2\text{kJ}) + \Delta\overline{\boldsymbol{H}}^0_f(\boldsymbol{Na}^+(\boldsymbol{aq})) + \; (-167.2 \; \text{kJ})$$

$$\Delta\overline{\boldsymbol{H}}^0_f(\boldsymbol{Na}^+(\boldsymbol{aq})) = \; -240.1 \; \text{kJ mol}^{-1}$$

Substance	ΔH^0_f (kJ mol^{-1})
$Al^{3+}(aq)$	-538.4
$Ba^{2+}(aq)$	-537.6
$Br^-(aq)$	-121.6

etc.

$$\Delta H_{reaction}$$

reactants $\longrightarrow$ products

ΔH_{vap} ΔH_{sublim} $-\Delta H_{vap}$ $-\Delta H_{sublim}$

reactants (gas phase) $\longrightarrow$ products (gas phase)
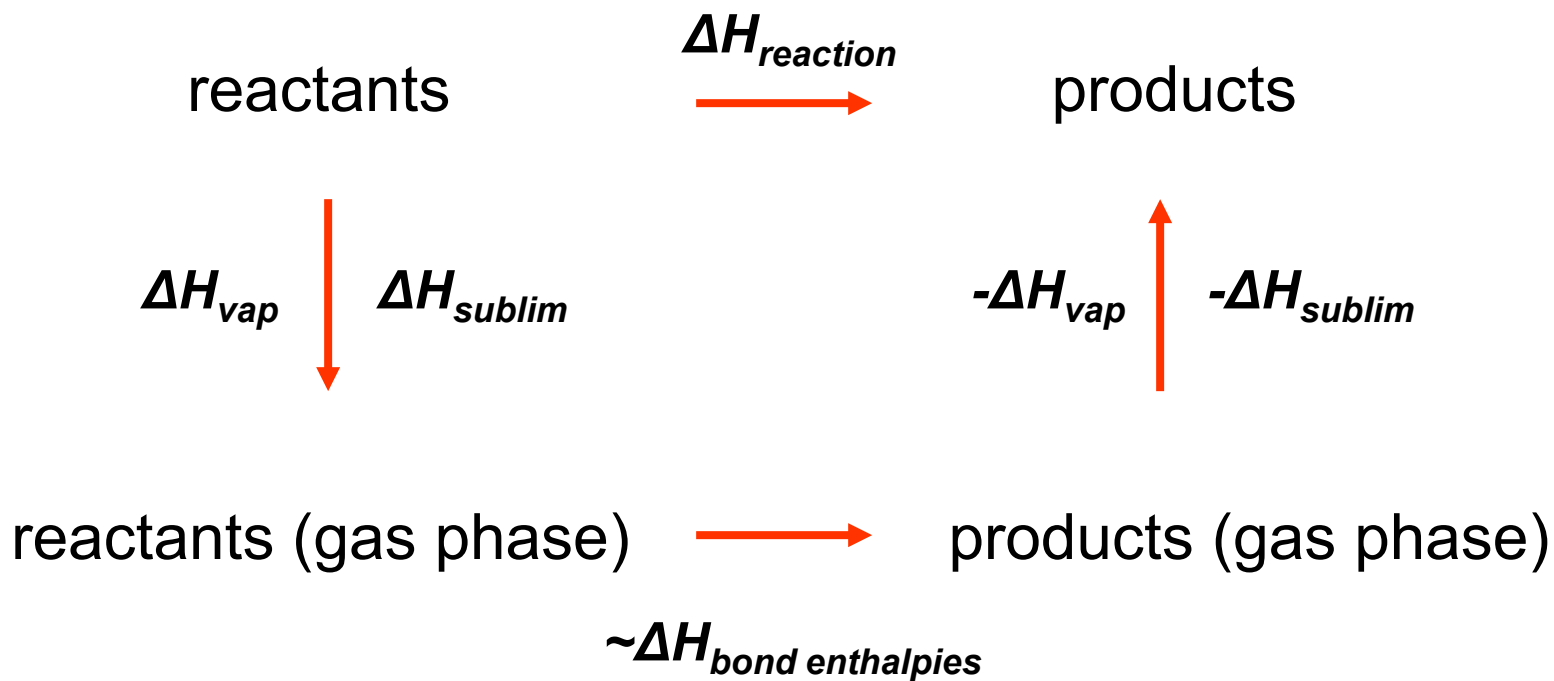
$\sim\Delta H_{bond\ enthalpies}$

- Similar bonds (C-H, C-C, C=C, C=O, etc) in similar molecule have similar enthalpies (energies)

- Use bond enthalpies (averaged over experimental data from several molecules) to approximate the enthalpies of the bonds broken in reactants and bonds formed in products to approximate **gas phase** $\Delta H_{reaction}$

reactants (gas phase) $\longrightarrow$ products (gas phase)

$$\Delta H = \sum \text{enthalpy bonds broken}$$

$$\Delta H > 0 \ \text{endothermic}$$

$$\Delta H = \sum \text{enthalpy bonds formed}$$

$$\Delta H < 0 \ \text{exothermic}$$

atoms in gas phase

ΔH_reaction *from bond enthalpies*

TABLE 8.4   Average Bond Enthalpies (kJ/mol)

Single Bonds

C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C—N	293	N—O	201	O—F	190	Cl—F	253
C—O	358	N—F	272	O—Cl	203	Cl—Cl	242
C—F	485	N—Cl	200	O—I	234		
C—Cl	328	N—Br	243			Br—F	237
C—Br	276			S—H	339	Br—Cl	218
C—I	240	H—H	436	S—F	327	Br—Br	193
C—S	259	H—F	567	S—Cl	253		
		H—Cl	431	S—Br	218	I—Cl	208
Si—H	323	H—Br	366	S—S	266	I—Br	175
Si—Si	226	H—I	299			I—I	151
Si—C	301						
Si—O	368						

Multiple Bonds

C=C	614	N=N	418	O$_2$	495
C≡C	839	N≡N	941		
C=N	615	N=O	607	S=O	523
C≡N	891			S=S	418
C=O	799				
C≡O	1072				

http://wps.prenhall.com/wps/media/objects/165/169060/tool0801.gif

example ΔH$_f$ CH$_3$CH=CH$_2$(g)

ΔH$_f$:   3C(gr) + 3H$_2$ (g) → CH$_3$CH=CH$_2$(g)

$3\overline{\Delta H}_{sub}(C)=3(717)$ kJ

ΔH$_{gas\ phase}$: 3C(g) + 3H$_2$ (g) → CH$_3$CHCH$_2$(g)
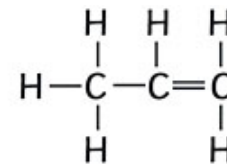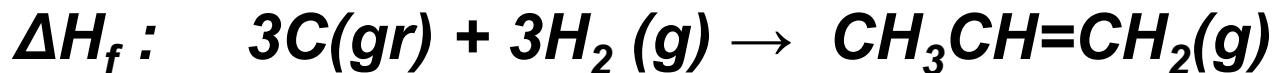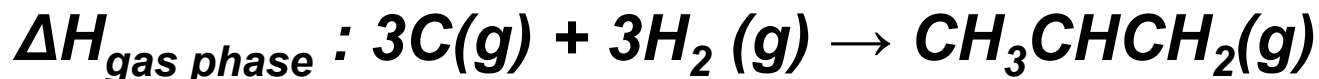
ΔH=3BE(H$_2$)
= 3 (436kJ)

ΔH=−6BE(C-H)−BE(C-C) −BE(C=C)
=− 6 (413kJ) − (348kJ) − (614kJ)

3C(g) + 6H (g)

ΔH$_f$= (3×717 + 3×436 − 6×413 − 348 − 614)kJ= **19** kJ

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example ΔH$_f$ CH$_3$CH=CH$_2$(g)

ΔH$_f$:   3C(gr) + 3H$_2$ (g) → CH$_3$CH=CH$_2$(g)

$3\overline{\Delta H}_{sub}(C)=3(717)$ kJ

ΔH$_{gas\ phase}$: 3C(g) + 3H$_2$ (g) → CH$_3$CHCH$_2$(g)
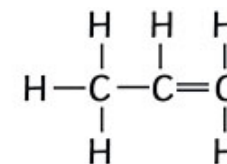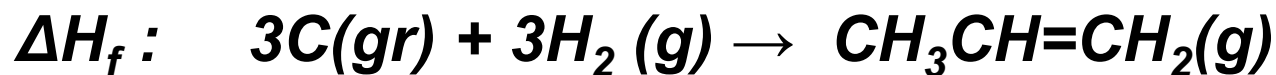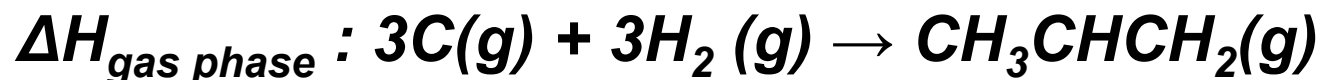
ΔH=3BE(H$_2$)

ΔH=−6BE(C-H)−BE(C-C) −BE(C=C)

TABLE 4.2   THERMODYNAMIC DATA FOR SELECTED ORGA

Substance	Formula	Molecular Weight	ΔH_f° (kJ mol^{-1})
Propene(g)	C$_3$H$_6$	42.08	20.0

- often [mis]used interchangeably
  Usually both meant to mean bond **enthalpy**

- bond **enthalpy:** thermodynamic heat measured
  at const P

- bond **energy:** the bond strength from quantum
  mechanical calculation

- can be interconverted by the $\Delta H = \Delta U + \Delta n_{gas}RT$
  relation (p. 92 [68]3rd; example problem 4.1 for O-H bond
  bond energy= 461 kJ mol^{-1} vs bond enthalpy=463.5 kJ mol^{-1})

- Table 4.3 E&R is weird (hard to read)

table 4.3 E&R

TABLE 4.3 MEAN BOND ENERGIES

1	2	Selected Bond Energies (kJ/mol)	13	14	15	16	17	18
H,2.20 432 --- 432 459 565								**He**
Li,0.98 105 --- 243 --- 573	**Be**,1.57 208 --- --- ---,444 632		**B**,2.04 293 --- 389 536,636 613	**C**,2.55 346 602,835 411 358,799 485	**N**,3.04 167 418,942 386 201,607 283	**O**,3.44 142 494 459 142,494 190	**F**,3.98 155 --- 565 --- 155	**Ne**
Na,0.93 72 --- 197 --- 477	**Mg**,1.31 129 --- --- ---,377 513		**Al**,1.61 --- --- 272 --- 583	**Si**,1.90 222 318 318 452,640 565	**P**,2.19 ~220 ---,481 322 335,544 490	**S**,2.58 240 425 363 ---,523 284	**Cl**,3.16 240 --- 428 218 249	**Ar**
K,0.82 49 --- 180 --- 490	**Sr**,1.00 105 --- --- ---,460 550		**Ga**,1.81 113 --- --- --- ~469	**Ge**,2.01 188 272 --- --- ~470	**As**,2.18 146 ---,380 247 301,389 ~440	**Se**,2.55 172 272 276 --- ~351	**Br**,2.96 190 --- 362 201 250	**Kr** 50
Rb,0.82 45 --- 163 --- 490	**Sr**,0.95 84 --- --- ---,347 553		**In**,1.78 100 --- --- --- ~523	**Sn**,1.80 146 --- --- --- ~450	**Sb**,2.05 121 ---,295 --- --- ~420	**Te**,2.10 126 218 238 --- ~393	**I**,2.66 149 --- 295 201 278	**Xe** 84 ~131
Cs,0.79 44 --- 176 --- 502	**Ba**,0.89 44 --- --- 467,561 578		**Tl**,2.04 --- --- --- --- 439	**Pb**,2.33 --- --- --- --- ~360	**Bi**,2.02 ---,192 --- --- ~350	**Po**,2.00	**At**,2.20 116	**Rn**

KEY

Element symbol →	**C**,2.55	Electronegativity
	C—C 346	Single bond with self
C=C, C≡C	602,835	Double, triple bond with self
	H—C 411	Bond with H
O—C, O=C	358,799	Single, double bond with O
	C—F 485	Bond with F

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ΔH~reaction~ *from bond enthalpies*

TABLE 8.4   Average Bond Enthalpies (kJ/mol)

Single Bonds

C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C—N	293	N—O	201	O—F	190	Cl—F	253
C—O	358	N—F	272	O—Cl	203	Cl—Cl	242
C—F	485	N—Cl	200	O—I	234		
C—Cl	328	N—Br	243			Br—F	237
C—Br	276			S—H	339	Br—Cl	218
C—I	240	H—H	436	S—F	327	Br—Br	193
C—S	259	H—F	567	S—Cl	253		
		H—Cl	431	S—Br	218	I—Cl	208
		H—Br	366	S—S	266	I—Br	175
Si—H	323	H—I	299			I—I	151
Si—Si	226						
Si—C	301						
Si—O	368						

Multiple Bonds

C=C	614	N=N	418	O_2	495
C≡C	839	N≡N	941		
C=N	615	N=O	607	S=O	523
C≡N	891			S=S	418
C=O	799				
C≡O	1072				

http://wps.prenhall.com/wps/media/objects/165/169060/tool0801.gif

✔   • Calculate $\Delta H_{reaction}$
    Hess's Law, standard heats of formation

✔   • $\Delta H_{reaction}$ vs $\Delta U_{reaction}$

✔   • Temperature (and pressure) dependence
    of $\Delta H_{reaction}$

✔   • Calorimetry

✔   • Heats of solution

✔   • $\Delta H_{reaction}$ from bond enthalpies

MIDTERM 1

end of thermochemistry section !!!

on to the 2nd Law

16. E&R$_{4th}$ P4.33 If 4.206 g of ethanol, C2H5OH(l) is burned completely in a bomb calorimeter at 298.15 K, the heat produced is 124.34 kJ.

a. Calculate $\Delta H°_{combustion}$ for ethanol at 298.15 K.

b. Calculate $\Delta H°_f$ of ethanol at 298.15 K.

[for part b. use Appendix A (4.1) only; no peeking at A(4.2) !!]

combustion: $C_2H_5OH(\ell) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(\ell)$

a. $\Delta \overline{H}^0_{combustion}$

bomb calorimeter $\Rightarrow q_{??}$

measure   convert to

$q_v = \Delta\overline{U} \Rightarrow \Delta\overline{H}^0_{combustion}$

(assume pure liquids,

gases 1 bar partial pressure)

$$C_2H_5OH(\ell) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(\ell)$$
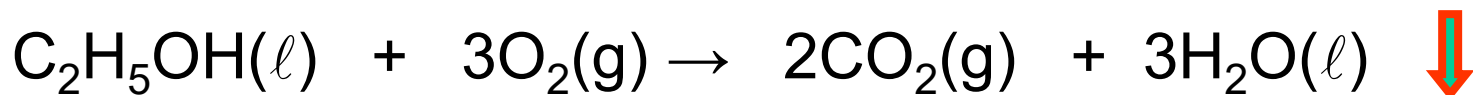
$\Delta \bar{H}^0_f:$ $\Delta \bar{H}^0_f(EtOH)$ 0 -393.5 -285.8 kJ mol^{-1}

$\Delta H^0_{comb} =$ $[(-1 \text{ mol})\Delta \bar{H}^0_f(EtOH) + (-3 \text{ mol})(0) + (2 \text{ mol})(-393.5\frac{kJ}{mol}) + (3 \text{ mol})(-285.8\frac{kJ}{mol})]$

$\sum_i \nu_i \left(\Delta \bar{H}^0_f\right)_i$

SOLVE FOR ΔH_f(EtOH)

$\Delta \bar{H}^0_f(EtOH) = [+ (2)(-393.5) + (\boldsymbol{3})(-285.8) - \Delta H^0_{comb}]\,\text{kJ mol}^{-1}$

$$\Delta \bar{H}^0_f(EtOH) = -279.7 \text{ kJ mol}^{-1}$$

TABLE 4.1 (CONTINUED)

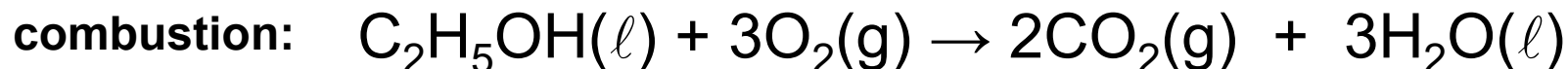| Substance	ΔH_f° (kJ mol^{-1})	ΔG_f° (kJ mol^{-1})	S° (J mol^{-1} K^{-1})	$C_{P,m}^\circ$ (J mol^{-1} K^{-1})	Atomic or Molecular Weight (amu)
H(g)	218.0	203.3	114.7	20.8	1.008
OH(g)	39.0	34.2	183.7	29.9	17.01
H$_2$O(g)	−241.8	−228.6	188.8	33.6	18.015
H$_2$O(l)	−285.8	−237.1	70.0	75.3	18.015
H$_2$O(s)			48.0	36.2 (273 K)	18.015
H$_2$O$_2$(g)	−136.3	−105.6	232.7	43.1	34.015
H$^+$(aq)	0	0	0		1.008
OH$^-$(aq)	−230.0	−157.24	−10.9		17.01
Carbon					
Graphite(s)	0	0	5.74	8.52	12.011
Diamond(s)	1.89	2.90	2.38	6.12	12.011
C(g)	716.7	671.2	158.1	20.8	12.011
CO(g)	−110.5	−137.2	197.7	29.1	28.011
CO$_2$(g)	−393.5	−394.4	213.8	37.1	44.010
HCN(g)	135.5	124.7	201.8	35.9	27.03
CN$^-$(aq)	150.6	172.4	94.1		26.02
HCO$_3^-$(aq)	−692.0	−586.8	91.2		61.02
CO$_3^{2-}$(aq)	−675.2	−527.8	−50.0		60.01
Oxygen					
O$_2$(g)	0	0	205.2	29.4	31.999
O(g)	249.2	231.7	161.1	21.9	15.999
O$_3$(g)	142.7	163.2	238.9	39.2	47.998
OH(g)	39.0	34.22	183.7	29.9	17.01
OH$^-$(aq)	−230.0	−157.2	−10.9		17.01

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16. E&R$_{4th}$ P4.33 If 4.206 g of ethanol, C2H5OH(l) is burned completely in a bomb calorimeter at 298.15 K, the heat produced is 124.34 kJ.

a. Calculate $\Delta H°_{combustion}$ for ethanol at 298.15 K.

b. Calculate $\Delta H°_f$ of ethanol at 298.15 K.

*[for part b. use Appendix A (4.1) only; no peeking at A(4.2) !!]*

TABLE 4.1 (CONTINUED)

Substance	ΔH_f° (kJ mol^{-1})	ΔG_f° (kJ mol^{-1})	S° (J mol^{-1} K^{-1})	$C_{P,m}^\circ$ (J mol^{-1} K^{-1})	Atomic or Molecular Weight (amu)
H(g)	218.0	203.3	114.7	20.8	1.008
OH(g)	39.0	34.2	183.7	29.9	17.01
H_2O(g)	−241.8	−228.6	188.8	33.6	18.015
H_2O(l)	−285.8	−237.1	70.0	75.3	18.015
H_2O(s)			48.0	36.2 (273 K)	18.015
H_2O_2(g)	−136.3	−105.6	232.7	43.1	34.015
H^+(aq)	0	0	0		1.008
OH^-(aq)	−230.0	−157.24	−10.9		17.01
Carbon					
Graphite(s)	0	0	5.74	8.52	12.011
Diamond(s)	1.89	2.90	2.38	6.12	12.011
C(g)	716.7	671.2	158.1	20.8	12.011
CO(g)	−110.5	−137.2	197.7	29.1	28.011
CO_2(g)	−393.5	−394.4	213.8	37.1	44.010
HCN(g)	135.5	124.7	201.8	35.9	27.03
CN^-(aq)	150.6	172.4	94.1		26.02
HCO_3^-(aq)	−692.0	−586.8	91.2		61.02
CO_3^{2-}(aq)	−675.2	−527.8	−50.0		60.01
Oxygen					
O_2(g)	0	0	205.2	29.4	31.999
O(g)	249.2	231.7	161.1	21.9	15.999
O_3(g)	142.7	163.2	238.9	39.2	47.998
OH(g)	39.0	34.22	183.7	29.9	17.01
OH^-(aq)	−230.0	−157.2	−10.9		17.01

TABLE 4.2 THERMODYNAMIC DATA FOR SELECTED ORGANIC COMPOUNDS AT 298.15 K

Substance	Formula	Molecular Weight	ΔH_f° (kJ mol^{-1})	$\Delta H_{combustion}^\circ$ (kJ mol^{-1})	ΔG_f° (kJ mol^{-1})	S° (J mol^{-1} K^{-1})	$C_{P,m}^\circ$ (J mol^{-1} K^{-1})
Carbon (graphite)	C	12.011	0	−393.5	0	5.74	8.52
Carbon (diamond)	C	12.011	1.89	−395.4	2.90	2.38	6.12
Carbon monoxide	CO	28.01	−110.5	−283.0	−137.2	197.7	29.1
Acetone(*l*)	C$_3$H$_6$O	58.08	−248.4	−1790	−155.2	199.8	126.3
Benzene(*l*)	C$_6$H$_6$	78.12	49.1	−3268	124.5	173.4	136.0
Benzene(*g*)	C$_6$H$_6$	78.12	82.9	−3303	129.7	269.2	82.4
Benzoic acid(*s*)	C$_7$H$_6$O$_2$	122.13	−385.2	−3227	−245.5	167.6	146.8
1,3-Butadiene(*g*)	C$_4$H$_6$	54.09	110.0	−2541			79.8
Dimethyl ether(*g*)	C$_2$H$_6$O	131.6	−184.1	−1460	−112.6	266.4	64.4
Ethane(*g*)	C$_2$H$_6$	30.07	−84.0	−1561	−32.0	229.2	52.5
Ethanol(*l*)	C$_2$H$_6$O	46.07	−277.6	−1367	−174.8	160.7	112.3
Ethanol(*g*)	C$_2$H$_6$O	46.07	−234.8	−1367	−167.9	281.6	65.6
Ethene(*g*)	C$_2$H$_4$	28.05	52.4	−1411	68.4	219.3	42.9
Ethyne(*g*)	C$_2$H$_2$	26.04	227.4	−1310	209.2	200.9	44
Formaldehyde(*g*)	CH$_2$O	30.03	−108.6	−571	−102.5	218.8	35.4

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standard state (º):   gas   partial pressure 1 bar

liquid or solid   pure substance at 1 bar

solute in soln   1 M (molar) [~ 1m (molal)]

standard molar heat of formation ($\overline{H}_f$º or $\Delta \overline{H}_f$º):

$(\Delta H_T$º$)_{reaction}$ where 1 mole of substance is produced from **elements in their most stable form at given temperature**

(some texts, e.g. E&R$_{4th}$,say T=298° also part of definition)

$$\Delta \overline{\boldsymbol{H}}_f^0 \text{ at } 298K \text{ in kJ/mol}$$

C(gr)=0 O$_2$(g)=0 C(dia)=1.89 H$_2$O(g)=-241.8 H$_2$O(ℓ)=-285.8

F$_2$(g)=0   Cl$_2$(g)=0   I$_2$(g)=62.4 I$_2$(s)=0