

# Chemistry 163B Winter 2014

## Lectures 6-7 Thermochemistry

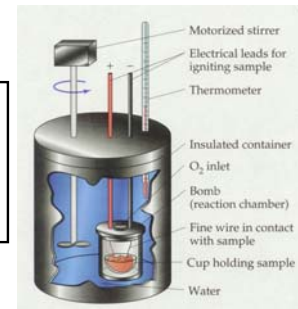
Chemistry 163B  
Thermochemistry  
Chapter 4 Engel & Reid

1

heats of reactions (constant volume; 'bomb' calorimeter)

$$\Delta U_V = q_V$$

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



2

heats of reactions (constant volume; fig 4.3 E&R)

$$\Delta U_V = q_V$$

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

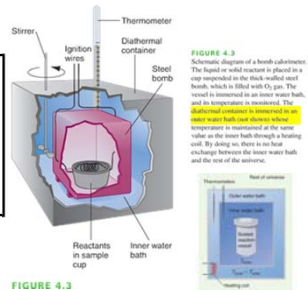


FIGURE 4.3

**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<sub>2</sub> gas. The vessel is immersed in an inner water bath, and its temperature is measured. The diathermal container is immersed in an outer water bath over electrical heating coils. 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 system.

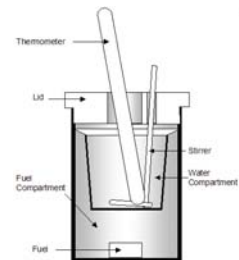
**FIGURE 4.4** The isolated reaction system is placed in a vessel in which the enthalpy in the system of interest is held constant. The water surrounding the inner reaction bath is liquid.

3

heats of reactions (constant pressure; 'coffee cup calorimeter')

$$\Delta H_P = q_P$$

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

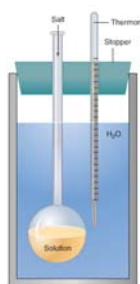


4

heats of reactions (constant pressure; fig 4.4 E&R)

$$\Delta H_P = q_P$$

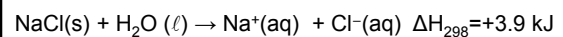
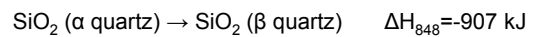
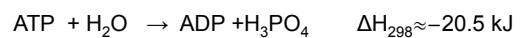
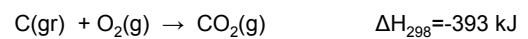
$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$



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

5

most reactions at P constant,  $\Delta H_P = q_P$



6

# Chemistry 163B Winter 2014

## Lectures 6-7 Thermochemistry

topics for thermochemistry, parts of Ch. 4 Engel & Reid

- HW#3 16 • Calculate  $\Delta H_{\text{reaction}}$
- HW#4 17,18 • Hess's Law, standard heats of formation
- HW#3 16 •  $\Delta H_{\text{reaction}}$  vs  $\Delta U_{\text{reaction}}$
- HW#4 18, \*19 • Temperature (and later pressure) dependence of  $\Delta H_{\text{reaction}}$
- Calorimetry
- Heats of solution
- HW#4 20, 21 •  $\Delta H_{\text{reaction}}$  from bond enthalpies

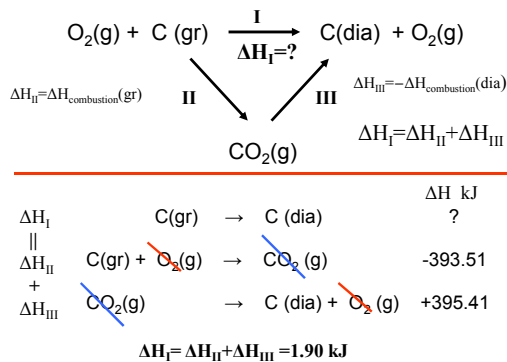
MIDTERM 1 7

Hess's Law

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

8

$\Delta H$  State Function  $\Rightarrow$  Hess's Law



9

factors affecting  $\Delta H_{\text{reaction}}$

- stoichiometry  
 $\Delta H$  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

10

notation:  $\Delta H$  (etc) in terms of molar enthalpies and stoichiometric coefficients



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

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

$$\Delta H_{\text{reaction}} = \sum_i v_i \bar{H}_i$$

$v_i$  is stoichiometric coefficient of  $i^{\text{th}}$  reactant / product

$v_i = n_i$  if  $i$  is product species

$v_i = -n_i$  if  $i$  is reactant species

11

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

$$H \equiv U + PV$$

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

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

assume:

- PV and  $\Delta PV$  is small for solids and liquids
- Gases follow ideal gas law

$$\Delta PV = (PV)_{\text{prods}} - (PV)_{\text{reacts}}$$

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

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

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

E&R eqn 4.25

12

# Chemistry 163B Winter 2014

## Lectures 6-7 Thermochemistry

standard states and enthalpies of formation

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

often  $T$  is assumed 298K for standard state  $\Delta H^\circ_{298}$

define standard states  $\Rightarrow$

$(\Delta \bar{H}^\circ_{298})_{\text{formation}} \equiv \bar{H}_f^\circ$  molar enthalpy of formation

define enthalpy of formation  $\Rightarrow$

13

$\Delta H^\circ_{\text{rxn}}$  from  $H_f^\circ$

reactants  $\rightarrow$  products

$(-\Delta H_f^\circ)_{\text{reactants}}$   $(\Delta H_f^\circ)_{\text{products}}$

elements in most stable state

$(\Delta H^\circ)_{\text{rxn}} = \sum_i \nu_i (\bar{H}_f^\circ)_i$

do HW#3 problem 16b (E&R 4.20b)

14

topics for thermochemistry, parts of Ch. 4 E&R

- ✓ Calculate  $\Delta H_{\text{reaction}}$   
Hess's Law, standard heats of formation
- ✓  $\Delta H_{\text{reaction}}$  vs  $\Delta U_{\text{reaction}}$
- Temperature (and pressure) dependence of  $\Delta H_{\text{reaction}}$
- Calorimetry
- Heats of solution
- $\Delta H_{\text{reaction}}$  from bond enthalpies

----- MIDTERM 1 -----

15

temperature dependence of  $H$  of substance at constant  $P$

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

for a given reactant or product at constant  $P$   
 $dH_p = n\bar{C}_p dT \quad d\bar{H}_p = \bar{C}_p dT$

change in enthalpy of substance  $T_1 \rightarrow T_2$

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

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

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

16

temperature dependence of  $\Delta H_{\text{reaction}}$  (reaction carried out at constant  $P, T$ )

$\Delta H_{\text{reaction}} = \sum_i \nu_i \bar{H}_i$   $\Delta H_{\text{rxn}}(T_1, P)$

vs  $\Delta H_{\text{rxn}}(T_2, P)$

$\bar{H}_i(T_2) = \bar{H}_i(T_1) + \int_{T_1}^{T_2} \bar{C}_{p,i} dT$

$\Delta H_{\text{reaction}}(T_2) = \sum_i \nu_i \bar{H}_i(T_2)$

$\sum_i \nu_i \bar{H}_i(T_2) = \sum_i \nu_i \bar{H}_i(T_1) + \sum_i \nu_i \int_{T_1}^{T_2} \bar{C}_{p,i} dT$

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

change of  $\Delta H_{\text{rxn}}$   $T_1 \rightarrow T_2$

where  $\Delta C_p = \sum_i \nu_i (\bar{C}_p)_i = \sum (\bar{C}_p)_{\text{products}} - \sum (\bar{C}_p)_{\text{reactants}}$

17

example problems :  $\Delta H$  from  $H_f^\circ$  and  $\Delta H T=298K \rightarrow 398K$

$3\text{C}_2\text{H}_2(\text{g}) \rightarrow \text{C}_6\text{H}_6(\ell)$  calc  $\Delta H^\circ_{298}$

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

$(\Delta H^\circ)_{298} = -3(227.4) + 1(49.1) = -633.1 \text{ kJ [per mol C}_6\text{H}_6(\ell)]$

$(\text{mol})(\text{kJ mol}^{-1}) + (\text{mol})(\text{kJ mol}^{-1}) = \text{kJ}$

---

$3\text{C}_2\text{H}_2(\text{g}) \rightarrow \text{C}_6\text{H}_6(\ell)$  calc  $\Delta H^\circ_{398}$

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

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

$(\Delta H^\circ)_{398} = (\Delta H^\circ)_{298} + \int_{298}^{398} \Delta C_p dT = (\Delta H^\circ)_{298} + \Delta C_p \Delta T$   $C_p$  independent of  $T$

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

18

# Chemistry 163B Winter 2014

## Lectures 6-7 Thermochemistry

### topics for thermochemistry, parts of Ch. 4 E&R

- ✓ Calculate  $\Delta H_{\text{reaction}}$   
Hess's Law, standard heats of formation
- ✓  $\Delta H_{\text{reaction}}$  vs  $\Delta U_{\text{reaction}}$
- ✓ Temperature (and pressure) dependence of  $\Delta H_{\text{reaction}}$
- Calorimetry
- Heats of solution
- $\Delta H_{\text{reaction}}$  from bond enthalpies

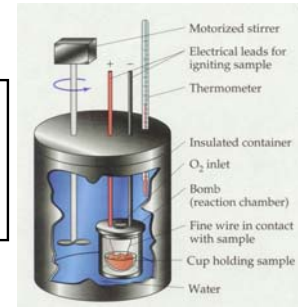
MIDTERM 1

19

### heats of reactions (constant volume)

$$\Delta U_v = q_v$$

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

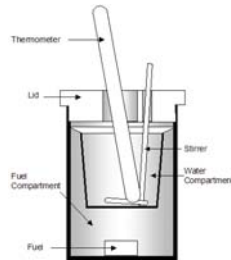


20

### heats of reactions (constant pressure)

$$\Delta H_p = q_p$$

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



21

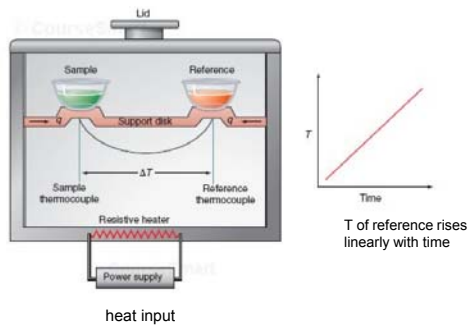
### DSC- differential scanning calorimetry (enrichment, don't FRET)



useful for small samples (often biological)

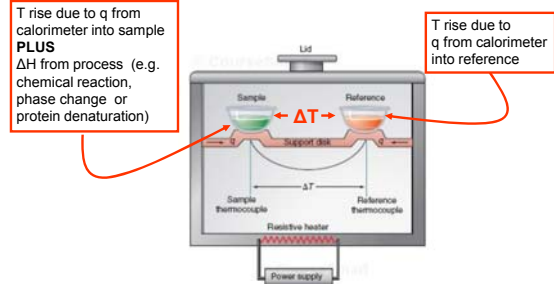
22

### DTA differential thermal analysis DSC differential scanning calorimetry



23

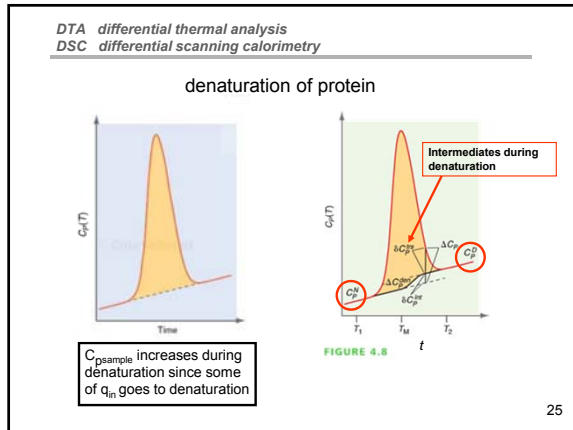
### DTA differential thermal analysis DSC differential scanning calorimetry



24

# Chemistry 163B Winter 2014

## Lectures 6-7 Thermochemistry



how  $H$  and  $\Delta H$  change with pressure (don't FRET now)

will prove later:

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

$$\alpha = \frac{1}{\bar{V}} \left(\frac{\partial \bar{V}}{\partial T}\right)_P \text{ the coefficient of thermal expansion}$$

$$\left(\frac{\partial \Delta H_{\text{reaction}}}{\partial P}\right)_T = \sum_i \nu_i (\bar{V}_i - T\bar{V}_i \alpha_i)$$

Will show later:

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

26

heats of formation of ions (heat of solutions), Example 4.4 p 73

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

resolution: assign  $\bar{H}_f^0(\text{H}^+(\text{aq}, 1\text{M})_{\text{ideal}}) = 0$  and measure  $\bar{H}_f^0$  for other ions relative to  $\text{H}^+$

27

heats of formation of ions (heat of solutions)

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

$$\text{HCl}(g, 1 \text{ bar}) \xrightarrow{-H_2O} \text{H}^+(\text{aq}, 1\text{M})_{\text{ideal}} + \text{Cl}^-(\text{aq}, 1\text{M})_{\text{ideal}}$$

$$\Delta H_{\text{measured}} = -74.9 \text{ kJ}$$

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

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

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

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

28

heats of formation of ions (heat of solutions)

**GET  $\bar{H}_f^0$  for  $\text{Na}^+(\text{aq})$**

$$\text{NaCl}(s) \xrightarrow{-H_2O} \text{Na}^+(\text{aq}, 1\text{M})_{\text{ideal}} + \text{Cl}^-(\text{aq}, 1\text{M})_{\text{ideal}}$$

$$\Delta H_{\text{measured}} = +3.89 \text{ kJ}$$

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

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

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

Substance	$\Delta H_f^0$ (kJ mol <sup>-1</sup> )
$\text{Al}^{3+}(\text{aq})$	-538.4
$\text{Ba}^{2+}(\text{aq})$	-537.6
$\text{Br}^-(\text{aq})$	-121.6

etc.

29

$\Delta H_{\text{reaction}}$  from bond enthalpies (p. 69)

reactants  $\xrightarrow{\Delta H_{\text{reaction}}}$  products

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

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

30

# Chemistry 163B Winter 2014

## Lectures 6-7 Thermochemistry

### $\Delta H_{\text{reaction}}$ from 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**  $\Delta H_{\text{reaction}}$

31

### $\Delta H_{\text{reaction}}$ from bond enthalpies

reactants (gas phase)  $\rightarrow$  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

32

### $\Delta H_{\text{reaction}}$ from bond enthalpies

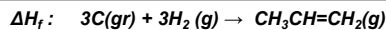
TABLE B.4 Average Bond Enthalpies (kJ/mol)

Single Bonds			
C-H	413	N-H	391
C-C	348	N-N	163
C-N	293	N-O	201
C-O	358	N-F	272
C-F	485	N-Cl	200
C-Cl	328	N-Br	243
C-Br	276	N-I	243
C-I	240	H-H	436
C-S	259	H-F	567
Si-H	323	H-Cl	431
Si-S	226	H-Br	366
Si-C	301	H-I	299
Si-O	368	S-H	339
		S-F	327
		S-Cl	253
		S-Br	218
		S-I	151
Multiple Bonds			
C=C	614	N=N	418
C#C	839	N#N	941
C=N	615	N=O	607
C#N	891	S=O	523
C=O	799	S=S	418
C=O	1072		

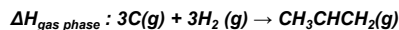
<http://wps.prenhall.com/wps/media/objects/165/169060/tool0801.gif>

33

### example $\Delta H_f$ $\text{CH}_3\text{CH}=\text{CH}_2(\text{g})$

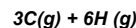


$$3\Delta \bar{H}_{\text{sub}}(\text{C}) = 3(717) \text{ kJ}$$



$$\Delta H = 3\text{BE}(\text{H}_2) = 3(436 \text{ kJ})$$

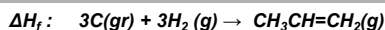
$$\Delta H = -6\text{BE}(\text{C-H}) - \text{BE}(\text{C-C}) - \text{BE}(\text{C=C}) = -6(413 \text{ kJ}) - (348 \text{ kJ}) - (614 \text{ kJ})$$



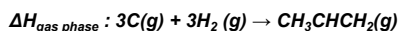
$$\Delta H_f = (3 \times 717 + 3 \times 436 - 6 \times 413 - 348 - 614) \text{ kJ} = 19 \text{ kJ}$$

34

### example $\Delta H_f$ $\text{CH}_3\text{CH}=\text{CH}_2(\text{g})$



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



$$\Delta H = 3\text{BE}(\text{H}_2)$$

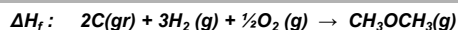
$$\Delta H = -6\text{BE}(\text{C-H}) - \text{BE}(\text{C-C}) - \text{BE}(\text{C=C})$$

TABLE 4.2 THERMODYNAMIC DATA FOR SELECTED ORGANIC COMPOUNDS

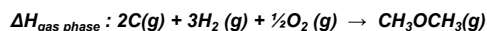
Substance	Formula	Molecular Weight	$\Delta H_f^\circ$ (kJ mol <sup>-1</sup> )
Propene(g)	C <sub>3</sub> H <sub>6</sub>	42.08	20.0

35

### example $\Delta H_f$ $\text{CH}_3\text{OCH}_3(\text{g})$



$$2\Delta \bar{H}_{\text{sub}}(\text{C}) = 2(717) \text{ kJ}$$



$$\Delta H = 3\text{BE}(\text{H}_2) + \frac{1}{2}\text{BE}(\text{O}_2) = 3(436 \text{ kJ}) + \frac{1}{2}(495 \text{ kJ})$$

$$\Delta H = -6\text{BE}(\text{C-H}) - 2\text{BE}(\text{C-O}) = -6(413 \text{ kJ}) - 2(358 \text{ kJ})$$



$$\Delta H_f = (2 \times 717 + 3 \times 436 + \frac{1}{2} \times 495 - 6 \times 413 - 2 \times 358) \text{ kJ} = -184.1 \text{ kJ}$$

Substance	Formula	Molecular Weight	$\Delta H_f^\circ$ (kJ mol <sup>-1</sup> )
Dimethyl ether(g)	C <sub>2</sub> H <sub>6</sub> O	131.6	-184.1

36

# Chemistry 163B Winter 2014

## Lectures 6-7 Thermochemistry

### bond enthalpy vs bond energy

- often [mis]used interchangeably  
Usually both meant to mean **enthalpy**
- bond **enthalpy**: thermodynamic heat measured at const P
- bond **energy**: the bond strength from quantum mechanical calculation
- can be interconverted by the  $\Delta H = \Delta U + \Delta n_{\text{gas}}RT$  relation (p. 68; example problem 4.1 for O-H bond *bond energy* =  $461 \text{ kJ mol}^{-1}$  vs *bond enthalpy* =  $463.5 \text{ kJ mol}^{-1}$ )
- Table 4.3 E&R is weird (hard to read)

37

table 4.3 E&R

TABLE 4.3 MEAN BOND ENERGIES

KEY

- Electron symbol:  $\sigma$  (sigma),  $\pi$  (pi)
- Color coding:  $\sigma$  (green),  $\pi$  (blue),  $\sigma$  (orange),  $\pi$  (purple),  $\sigma$  (yellow),  $\pi$  (pink)
- Legend:  $\sigma$  (green),  $\pi$  (blue),  $\sigma$  (orange),  $\pi$  (purple),  $\sigma$  (yellow),  $\pi$  (pink)

38

### topics for thermochemistry, parts of Ch. 4 E&R

- ✓ • Calculate  $\Delta H_{\text{reaction}}$   
Hess's Law, standard heats of formation
- ✓ •  $\Delta H_{\text{reaction}}$  vs  $\Delta U_{\text{reaction}}$
- ✓ • Temperature (and pressure) dependence of  $\Delta H_{\text{reaction}}$
- ✓ • Calorimetry
- ✓ • Heats of solution
- ✓ •  $\Delta H_{\text{reaction}}$  from bond enthalpies

----- MIDTERM 1 -----

39

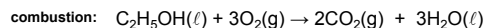
end of thermochemistry section !!!  
on to the 2<sup>nd</sup> Law

40

### E&R prob 4.20 HW#3 16

**P4.20** If 3.365 g of ethanol  $\text{C}_2\text{H}_5\text{OH}(l)$  is burned completely in a bomb calorimeter at 298.15 K, the heat produced is 99.472 kJ.

- Calculate  $\Delta H_{\text{combustion}}^\circ$  for ethanol at 298.15 K.
  - Calculate  $\Delta H_f^\circ$  of ethanol at 298.15 K.
- [for part b. use Appendix A (4.1) only; no peeking at A(4.2) !!]



a.  $\Delta \bar{H}_{\text{combustion}}^\circ$

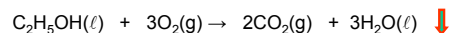
bomb calorimeter  $\Rightarrow q_v$

$$q_v = \Delta \bar{U} \Rightarrow \Delta \bar{H}_{\text{combustion}}^\circ$$

(assume pure liquids,  
gases 1 bar partial pressure)

41

### E&R prob 4.20b HW3 #16 (cont) using $\Delta H_{\text{comb}}^\circ$ from 4.20a



$$\bar{H}_f^\circ: \quad \bar{H}_f^\circ(\text{EtOH}) \quad 0 \quad -393.5 \quad -285.8 \text{ kJ mol}^{-1}$$

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

SOLVE FOR  $H_f(\text{EtOH})$

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

$$\bar{H}_f^\circ(\text{EtOH}) = -279.7 \text{ kJ mol}^{-1} \quad \uparrow$$

42

# Chemistry 163B Winter 2014

## Lectures 6-7 Thermochemistry

**TABLE 4.1 (CONTINUED)**

Substance	$\Delta H_f^\circ$ (kJ mol <sup>-1</sup> )	$\Delta G_f^\circ$ (kJ mol <sup>-1</sup> )	$S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$C_{p,m}$ (J mol <sup>-1</sup> K <sup>-1</sup> )	Atomic or Molecular Weight (amu)
H <sub>2</sub> (g)	218.0	203.3	114.7	20.8	1.008
OH <sub>2</sub> (g)	39.0	34.2	183.7	29.9	17.01
H <sub>2</sub> O(g)	-241.8	-228.6	188.8	33.6	18.015
H <sub>2</sub> O(l)	-285.8	-237.1	70.0	75.3	18.015
H <sub>2</sub> O(s)	-285.8	-237.1	48.0	36.2 (273 K)	18.015
H <sub>2</sub> O <sub>2</sub> (g)	-136.3	-105.6	232.7	43.1	34.015
H <sup>+</sup> (aq)	0	0	0	0	1.008
OH <sup>-</sup> (aq)	-230.0	-157.24	-10.9	17.01	17.01
<b>Carbon</b>					
Graphite(s)	0	0	5.74	8.52	12.011
Diamond(s)	1.89	2.90	2.38	6.12	12.011
C(s)	716.7	671.2	158.1	20.8	12.011
CO(g)	-110.5	-137.2	197.7	29.1	28.011
CO <sub>2</sub> (g)	-393.5	-394.4	213.8	37.1	44.010
HCN(g)	135.5	124.7	201.8	35.9	27.03
CN <sup>-</sup> (aq)	150.6	172.4	94.1	26.02	26.02
HCO <sub>2</sub> <sup>-</sup> (aq)	-692.0	-586.8	91.2	61.02	61.02
CO <sub>3</sub> <sup>2-</sup> (aq)	-675.2	-577.8	-50.0	60.01	60.01
<b>Oxygen</b>					
O <sub>2</sub> (g)	0	0	205.2	29.4	31.999
O(g)	249.2	231.7	161.1	21.9	15.999
O <sub>3</sub> (g)	142.7	163.2	238.9	39.2	47.998
OH <sub>2</sub> (g)	39.0	34.22	183.7	29.9	17.01
OH <sup>-</sup> (aq)	-230.0	-157.2	-10.9	17.01	17.01

43

E&R prob 4.20b HW3 #16

**P4.20** If 3.059 g of ethanol, C<sub>2</sub>H<sub>5</sub>OH(l) is burned completely in a bomb calorimeter at 298.15 K, the heat produced is 90.447 kJ.

a. Calculate  $\Delta H_f^\circ$  for ethanol at 298.15 K.  
 b. Calculate  $\Delta H_f^\circ$  of ethanol at 298.15 K.

44

**TABLE 4.1 (CONTINUED)**

Substance	$\Delta H_f^\circ$ (kJ mol <sup>-1</sup> )	$\Delta G_f^\circ$ (kJ mol <sup>-1</sup> )	$S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$C_{p,m}$ (J mol <sup>-1</sup> K <sup>-1</sup> )	Atomic or Molecular Weight (amu)
H <sub>2</sub> (g)	218.0	203.3	114.7	20.8	1.008
OH <sub>2</sub> (g)	39.0	34.2	183.7	29.9	17.01
H <sub>2</sub> O(g)	-241.8	-228.6	188.8	33.6	18.015
H <sub>2</sub> O(l)	-285.8	-237.1	70.0	75.3	18.015
H <sub>2</sub> O(s)	-285.8	-237.1	48.0	36.2 (273 K)	18.015
H <sub>2</sub> O <sub>2</sub> (g)	-136.3	-105.6	232.7	43.1	34.015
H <sup>+</sup> (aq)	0	0	0	0	1.008
OH <sup>-</sup> (aq)	-230.0	-157.24	-10.9	17.01	17.01
<b>Carbon</b>					
Graphite(s)	0	0	5.74	8.52	12.011
Diamond(s)	1.89	2.90	2.38	6.12	12.011
C(s)	716.7	671.2	158.1	20.8	12.011
CO(g)	-110.5	-137.2	197.7	29.1	28.011
CO <sub>2</sub> (g)	-393.5	-394.4	213.8	37.1	44.010
HCN(g)	135.5	124.7	201.8	35.9	27.03
CN <sup>-</sup> (aq)	150.6	172.4	94.1	26.02	26.02
HCO <sub>2</sub> <sup>-</sup> (aq)	-692.0	-586.8	91.2	61.02	61.02
CO <sub>3</sub> <sup>2-</sup> (aq)	-675.2	-577.8	-50.0	60.01	60.01
<b>Oxygen</b>					
O <sub>2</sub> (g)	0	0	205.2	29.4	31.999
O(g)	249.2	231.7	161.1	21.9	15.999
O <sub>3</sub> (g)	142.7	163.2	238.9	39.2	47.998
OH <sub>2</sub> (g)	39.0	34.22	183.7	29.9	17.01
OH <sup>-</sup> (aq)	-230.0	-157.2	-10.9	17.01	17.01

45

**TABLE 4.2 THERMODYNAMIC DATA FOR SELECTED ORGANIC COMPOUNDS AT 298.15 K**

Substance	Formula	Molecular Weight	$\Delta H_f^\circ$ (kJ mol <sup>-1</sup> )	$\Delta H_{combustion}^\circ$ (kJ mol <sup>-1</sup> )	$\Delta G_f^\circ$ (kJ mol <sup>-1</sup> )	$S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$C_{p,m}$ (J mol <sup>-1</sup> K <sup>-1</sup> )
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 <sub>3</sub> H <sub>6</sub> O	58.08	-248.4	-1790	-155.2	199.8	126.3
Benzene(l)	C <sub>6</sub> H <sub>6</sub>	78.12	-120.1	-3208	124.5	173.4	136.0
Benzene(g)	C <sub>6</sub> H <sub>6</sub>	78.12	82.9	-3303	129.7	269.2	82.4
Benzoic acid(s)	C <sub>7</sub> H <sub>6</sub> O <sub>2</sub>	122.13	-385.2	-3227	-245.5	167.6	146.8
1,3-Butadiene(g)	C <sub>4</sub> H <sub>6</sub>	54.09	110.0	-2541	-2541	201.7	79.8
Dimethyl ether(g)	C <sub>2</sub> H <sub>6</sub> O	46.07	-184.1	-1400	-112.6	266.4	64.4
Ethanol(g)	C <sub>2</sub> H <sub>6</sub> O	46.07	-84.0	-1367	-32.0	229.2	52.5
Ethanol(l)	C <sub>2</sub> H <sub>6</sub> O	46.07	-277.6	-1367	-174.8	160.7	112.3
Ethanol(s)	C <sub>2</sub> H <sub>6</sub> O	46.07	-234.8	-1367	-167.9	281.6	65.6
Ethene(g)	C <sub>2</sub> H <sub>4</sub>	28.05	52.4	-1411	68.4	219.3	42.9
Ethyne(g)	C <sub>2</sub> H <sub>2</sub>	26.04	227.4	-1310	209.2	200.9	44.1
Formaldehyde(g)	CH <sub>2</sub> O	30.03	-108.6	-571	-102.5	218.8	35.4

46

*standard states and standard heats of formation*

standard state (°): gas partial pressure 1 bar  
 liquid or solid pure substance at 1 bar  
 solute in soln 1 M

standard molar heat of formation ( $H_f^\circ$ ):  
 $(\Delta H_T^\circ)_{\text{reaction}}$  where 1 mole of substance is produced  
 from **elements in their most stable form at given temperature**

$\bar{H}_f^\circ$  at 298K in kJ/mol

$C(\text{gr})=0$   $O_2(\text{g})=0$   $C(\text{dia})=1.89$   $H_2O(\text{g})=-241.8$   $H_2O(\text{l})=-285.8$   
 $F_2(\text{g})=0$   $Cl_2(\text{g})=0$   $I_2(\text{g})=62.4$   $I_2(\text{s})=0$

47

*Raff Table 3.2 bond enthalpies*

3.3 Bond Enthalpies 135

Table 3.2 Average bond enthalpies in kJ mol <sup>-1</sup>										
	H	C	N	O	F	Cl	Br	I	S	P
H	436									
C	413	348(a)								
		612(d)								
		830(e)								
		518(ar)								
N	391	292(a)	361(a)							
		616(d)	413(d)							
		800(e)	940(e)							
O	463	350(a)	166	140(a)						
		734(d)		497(d)						
F	565	484	270	185	156					
Cl	431	323	200	200	254	243				
Br	366	276	200	200	239	193				
I	299	238			230	178	151			
S	303	259			496	250	212	265		
P	322								201	

(a) single bond, (d) double bond, (l) triple bond, (ar) aromatic bond  
 Data: Pauling, L. *General Chemistry*, 3rd ed., Freeman, San Francisco, 1970; Atlas, P. *Physical Chemistry*, 5th ed., Freeman, New York, 1964. Where the data differ, averages are taken.

48