

Chemistry 163B Winter 2014

Lectures 6-7 Thermochemistry

Chemistry 163B
Thermochemistry
Chapter 4 Engel & Reid

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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)

$$\Delta U_V = q_V$$

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

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)

$$\Delta H_P = q_P$$

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

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

$\text{C}(\text{gr}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$	$\Delta H_{298} = -393 \text{ kJ}$
$\text{ATP} + \text{H}_2\text{O} \rightarrow \text{ADP} + \text{H}_3\text{PO}_4$	$\Delta H_{298} \approx -20.5 \text{ kJ}$
$\text{SiO}_2 (\alpha \text{ quartz}) \rightarrow \text{SiO}_2 (\beta \text{ quartz})$	$\Delta H_{848} = -907 \text{ kJ}$
$\text{NaCl}(\text{s}) + \text{H}_2\text{O} (\ell) \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$	$\Delta H_{298} = +3.9 \text{ kJ}$

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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

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

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ΔH State Function \Rightarrow Hess's Law

ΔH kJ		ΔH kJ
ΔH_I	$\text{C}(\text{gr}) \rightarrow \text{C}(\text{dia})$?
ΔH_{II}	$\text{C}(\text{gr}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$	-393.51
ΔH_{III}	$\text{CO}_2(\text{g}) \rightarrow \text{C}(\text{dia}) + \text{O}_2(\text{g})$	+395.41
$\Delta H_I = \Delta H_{II} + \Delta H_{III} = 1.90 \text{ kJ}$		

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

- 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

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notation: ΔH (etc) in terms of molar enthalpies and stoichiometric coefficients

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

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

total enthalpy of reactants molar enthalpy of reactant i

number of moles of i in stoichiometry

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

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

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

$v_i = n_i$ if i is product species

$v_i = -n_i$ if i is reactant species

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$\Delta H_{\text{reaction}}$ 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 ΔPV is small for solids and liquids
- Gasses 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

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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 ΔH°_{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

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ΔH_{rxn} from H_f

reactants \rightarrow products

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

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)

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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 -----

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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
 $dH_p = n\bar{C}_p dT$ $d\bar{H}_p = \bar{C}_p dT$

change in enthalpy of substance $T_1 \rightarrow T_2$ $\left\{ \begin{array}{l} \int_{T_1}^{T_2} d\bar{H} = \int_{T_1}^{T_2} \bar{C}_p dT \\ \bar{H}(T_2) - \bar{H}(T_1) = \int_{T_1}^{T_2} \bar{C}_p dT \\ \bar{H}(T_2) = \bar{H}(T_1) + \int_{T_1}^{T_2} \bar{C}_p dT \end{array} \right.$

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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

$\bar{H}_i(T_2) = \bar{H}_i(T_1) + \int_{T_1}^{T_2} (\bar{C}_p)_i dT$ $\Delta H_{\text{rxn}}(T_2, P)$

$\Delta H_{\text{reaction}}(T_2) = \sum_i \nu_i \bar{H}_i(T_2) = \sum_i \nu_i \bar{H}_i(T_1) + \sum_i \nu_i \int_{T_1}^{T_2} (\bar{C}_p)_i dT$

$\Delta H_{\text{reaction}}(T_2) = \Delta H_{\text{reaction}}(T_1) + \int_{T_1}^{T_2} \sum_i \nu_i (\bar{C}_p)_i dT$ change of ΔH_{rxn} $T_1 \rightarrow T_2$

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

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

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

$3\text{C}_2\text{H}_2(\text{g}) \rightarrow \text{C}_6\text{H}_6(\text{l})$ calc ΔH°_{298} ↓

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

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

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

$3\text{C}_2\text{H}_2(\text{g}) \rightarrow \text{C}_6\text{H}_6(\text{l})$ calc ΔH°_{398} ↓

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

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

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

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

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

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 - Calorimetry
 - Heats of solution
 - $\Delta H_{\text{reaction}}$ from bond enthalpies

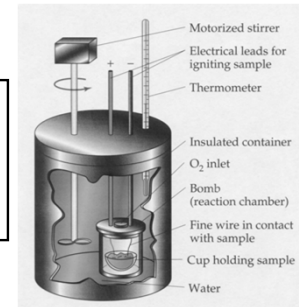
MIDTERM 1

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heats of reactions (constant volume)

$$\Delta U_v = q_v$$

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

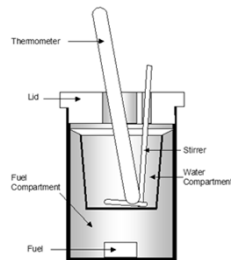


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heats of reactions (constant pressure)

$$\Delta H_p = q_p$$

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



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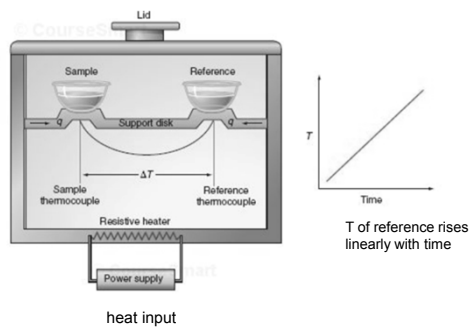
DSC- differential scanning calorimetry (enrichment, don't FRET)



useful for small samples (often biological)

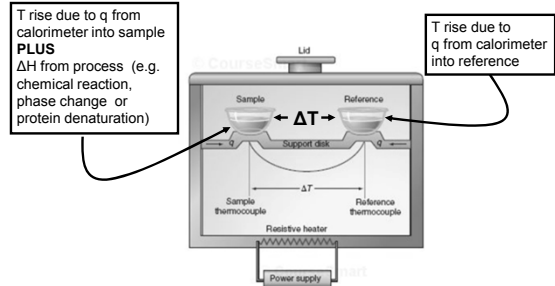
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DTA differential thermal analysis DSC differential scanning calorimetry



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DTA differential thermal analysis DSC differential scanning calorimetry



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DTA differential thermal analysis
DSC differential scanning calorimetry

denaturation of protein

FIGURE 4.8

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how H and ΔH change with pressure (don't FRET now)

will prove later:

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

$\alpha \equiv \frac{1}{\bar{V}} \left(\frac{\partial \bar{V}}{\partial T}\right)_P$ 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

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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 H^+

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heats of formation of ions (heat of solutions)

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

$$\text{HCl}(\text{g}, 1 \text{ bar}) \xrightarrow{\text{H}_2\text{O}} \text{H}^+(\text{aq}, 1\text{M})_{\text{ideal}} + \text{Cl}^-(\text{aq}, 1\text{M})_{\text{ideal}}$$

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

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

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

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

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

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heats of formation of ions (heat of solutions)

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

$$\text{NaCl}(\text{s}) \xrightarrow{\text{H}_2\text{O}} \text{Na}^+(\text{aq}, 1\text{M})_{\text{ideal}} + \text{Cl}^-(\text{aq}, 1\text{M})_{\text{ideal}}$$

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

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

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

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

Substance	ΔH_f^0 (kJ mol ⁻¹)
$\text{Al}^{3+}(\text{aq})$	-538.4
$\text{Ba}^{2+}(\text{aq})$	-537.6
$\text{Br}^-(\text{aq})$	-121.6

etc.

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

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

$$\Delta H_{\text{vap}} \downarrow \quad \Delta H_{\text{sublim}} \quad \uparrow \quad -\Delta H_{\text{vap}} \quad -\Delta H_{\text{sublim}}$$

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

~ $\Delta H_{\text{bond enthalpies}}$

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

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

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

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

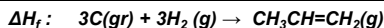
TABLE 8.4 Average Bond Enthalpies (kJ/mol)

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	S-H	339	Br-F	237
C-Br	276			S-F	327	Br-Cl	218
C-I	240	H-H	436	S-Cl	253	Br-Br	193
C-S	259	H-F	567	S-Br	218	I-Cl	208
Si-H	323	H-Cl	431	S-I	175	I-Br	175
Si-N	226	H-Br	366	S-S	266	I-I	151
Si-C	301	H-I	299				
Si-O	368						
Multiple Bonds							
C=C	614	N=N	418	O=O	495		
C≡C	839	N≡N	941				
C=N	615	N=O	607	S=O	523		
C≡N	891						
C=O	799	S=S	418				
C=O	1072						

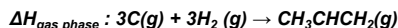
<http://wps.prenhall.com/wps/media/objects/165/169060/tool0801.gif>

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example ΔH_f $\text{CH}_3\text{CH}=\text{CH}_2(\text{g})$

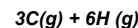


$$3\Delta \bar{H}_{\text{sub}}(\text{C}) = 3(717) \text{ kJ}$$



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

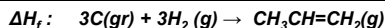
$$\Delta H = -6\text{BE}(\text{C-H}) - \text{BE}(\text{C-C}) - \text{BE}(\text{C=C}) = -6(413 \text{ kJ}) - (348 \text{ kJ}) - (614 \text{ kJ})$$



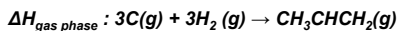
$$\Delta H_f = (3 \times 717 + 3 \times 436 - 6 \times 413 - 348 - 614) \text{ kJ} = 19 \text{ kJ}$$

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example ΔH_f $\text{CH}_3\text{CH}=\text{CH}_2(\text{g})$



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



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

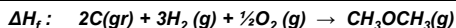
$$\Delta H = -6\text{BE}(\text{C-H}) - \text{BE}(\text{C-C}) - \text{BE}(\text{C=C})$$

TABLE 4.2 THERMODYNAMIC DATA FOR SELECTED ORGANIC COMPOUNDS

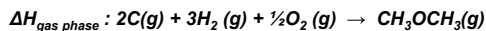
Substance	Formula	Molecular Weight	ΔH_f° (kJ mol ⁻¹)
Propene(g)	C ₃ H ₆	42.08	20.0

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example ΔH_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	ΔH_f° (kJ mol ⁻¹)
Dimethyl ether(g)	C ₂ H ₆ O	131.6	-184.1

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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 kJ mol⁻¹ vs *bond enthalpy* = 463.5 kJ mol⁻¹)
- Table 4.3 E&R is weird (hard to read)

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table 4.3 E&R

1	2	3	4	5	6	7	8
32.0	120	130	140	150	160	170	180
190	200	210	220	230	240	250	260
270	280	290	300	310	320	330	340
350	360	370	380	390	400	410	420
430	440	450	460	470	480	490	500
510	520	530	540	550	560	570	580
590	600	610	620	630	640	650	660
670	680	690	700	710	720	730	740
750	760	770	780	790	800	810	820
830	840	850	860	870	880	890	900
910	920	930	940	950	960	970	980
990	1000	1010	1020	1030	1040	1050	1060
1070	1080	1090	1100	1110	1120	1130	1140
1150	1160	1170	1180	1190	1200	1210	1220
1230	1240	1250	1260	1270	1280	1290	1300
1310	1320	1330	1340	1350	1360	1370	1380
1390	1400	1410	1420	1430	1440	1450	1460
1470	1480	1490	1500	1510	1520	1530	1540
1550	1560	1570	1580	1590	1600	1610	1620
1630	1640	1650	1660	1670	1680	1690	1700
1710	1720	1730	1740	1750	1760	1770	1780
1790	1800	1810	1820	1830	1840	1850	1860
1870	1880	1890	1900	1910	1920	1930	1940
1950	1960	1970	1980	1990	2000	2010	2020
2030	2040	2050	2060	2070	2080	2090	2100
2110	2120	2130	2140	2150	2160	2170	2180
2190	2200	2210	2220	2230	2240	2250	2260
2270	2280	2290	2300	2310	2320	2330	2340
2350	2360	2370	2380	2390	2400	2410	2420
2430	2440	2450	2460	2470	2480	2490	2500
2510	2520	2530	2540	2550	2560	2570	2580
2590	2600	2610	2620	2630	2640	2650	2660
2670	2680	2690	2700	2710	2720	2730	2740
2750	2760	2770	2780	2790	2800	2810	2820
2830	2840	2850	2860	2870	2880	2890	2900
2910	2920	2930	2940	2950	2960	2970	2980
2990	3000	3010	3020	3030	3040	3050	3060
3070	3080	3090	3100	3110	3120	3130	3140
3150	3160	3170	3180	3190	3200	3210	3220
3230	3240	3250	3260	3270	3280	3290	3300
3310	3320	3330	3340	3350	3360	3370	3380
3390	3400	3410	3420	3430	3440	3450	3460
3470	3480	3490	3500	3510	3520	3530	3540
3550	3560	3570	3580	3590	3600	3610	3620
3630	3640	3650	3660	3670	3680	3690	3700
3710	3720	3730	3740	3750	3760	3770	3780
3790	3800	3810	3820	3830	3840	3850	3860
3870	3880	3890	3900	3910	3920	3930	3940
3950	3960	3970	3980	3990	4000	4010	4020
4030	4040	4050	4060	4070	4080	4090	4100
4110	4120	4130	4140	4150	4160	4170	4180
4190	4200	4210	4220	4230	4240	4250	4260
4270	4280	4290	4300	4310	4320	4330	4340
4350	4360	4370	4380	4390	4400	4410	4420
4430	4440	4450	4460	4470	4480	4490	4500
4510	4520	4530	4540	4550	4560	4570	4580
4590	4600	4610	4620	4630	4640	4650	4660
4670	4680	4690	4700	4710	4720	4730	4740
4750	4760	4770	4780	4790	4800	4810	4820
4830	4840	4850	4860	4870	4880	4890	4900
4910	4920	4930	4940	4950	4960	4970	4980
4990	5000	5010	5020	5030	5040	5050	5060
5070	5080	5090	5100	5110	5120	5130	5140
5150	5160	5170	5180	5190	5200	5210	5220
5230	5240	5250	5260	5270	5280	5290	5300
5310	5320	5330	5340	5350	5360	5370	5380
5390	5400	5410	5420	5430	5440	5450	5460
5470	5480	5490	5500	5510	5520	5530	5540
5550	5560	5570	5580	5590	5600	5610	5620
5630	5640	5650	5660	5670	5680	5690	5700
5710	5720	5730	5740	5750	5760	5770	5780
5790	5800	5810	5820	5830	5840	5850	5860
5870	5880	5890	5900	5910	5920	5930	5940
5950	5960	5970	5980	5990	6000	6010	6020
6030	6040	6050	6060	6070	6080	6090	6100
6110	6120	6130	6140	6150	6160	6170	6180
6190	6200	6210	6220	6230	6240	6250	6260
6270	6280	6290	6300	6310	6320	6330	6340
6350	6360	6370	6380	6390	6400	6410	6420
6430	6440	6450	6460	6470	6480	6490	6500
6510	6520	6530	6540	6550	6560	6570	6580
6590	6600	6610	6620	6630	6640	6650	6660
6670	6680	6690	6700	6710	6720	6730	6740
6750	6760	6770	6780	6790	6800	6810	6820
6830	6840	6850	6860	6870	6880	6890	6900
6910	6920	6930	6940	6950	6960	6970	6980
6990	7000	7010	7020	7030	7040	7050	7060
7070	7080	7090	7100	7110	7120	7130	7140
7150	7160	7170	7180	7190	7200	7210	7220
7230	7240	7250	7260	7270	7280	7290	7300
7310	7320	7330	7340	7350	7360	7370	7380
7390	7400	7410	7420	7430	7440	7450	7460
7470	7480	7490	7500	7510	7520	7530	7540
7550	7560	7570	7580	7590	7600	7610	7620
7630	7640	7650	7660	7670	7680	7690	7700
7710	7720	7730	7740	7750	7760	7770	7780
7790	7800	7810	7820	7830	7840	7850	7860
7870	7880	7890	7900	7910	7920	7930	7940
7950	7960	7970	7980	7990	8000	8010	8020
8030	8040	8050	8060	8070	8080	8090	8100
8110	8120	8130	8140	8150	8160	8170	8180
8190	8200	8210	8220	8230	8240	8250	8260
8270	8280	8290	8300	8310	8320	8330	8340
8350	8360	8370	8380	8390	8400	8410	8420
8430	8440	8450	8460	8470	8480	8490	8500
8510	8520	8530	8540	8550	8560	8570	8580
8590	8600	8610	8620	8630	8640	8650	8660
8670	8680	8690	8700	8710	8720	8730	8740
8750	8760	8770	8780	8790	8800	8810	8820
8830	8840	8850	8860	8870	8880	8890	8900
8910	8920	8930	8940	8950	8960	8970	8980
8990	9000	9010	9020	9030	9040	9050	9060
9070	9080	9090	9100	9110	9120	9130	9140
9150	9160	9170	9180	9190	9200	9210	9220
9230	9240	9250	9260	9270	9280	9290	9300
9310	9320	9330	9340	9350	9360	9370	9380
9390	9400	9410	9420	9430	9440	9450	9460
9470	9480	9490	9500	9510	9520	9530	9540
9550	9560	9570	9580	9590	9600	9610	9620
9630	9640	9650	9660	9670	9680	9690	9700
9710	9720	9730	9740	9750	9760	9770	9780
9790	9800	9810	9820	9830	9840	9850	9860
9870	9880	9890	9900	9910	9920	9930	9940
9950	9960	9970	9980	9990	10000	10010	10020

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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

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end of thermochemistry section !!!

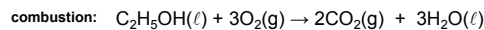
on to the 2nd Law

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E&R prob 4.20 HW#3 16

P4.20 If 3.365 g of ethanol C₂H₅OH(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 ΔH_f° 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 = q_v

$$

Chemistry 163B Winter 2014

Lectures 6-7 Thermochemistry

TABLE 4.1 (CONTINUED)

Substance	ΔH_f° (kJ mol ⁻¹)	ΔG_f° (kJ mol ⁻¹)	S° (J mol ⁻¹ K ⁻¹)	$C_{p,m}$ (J mol ⁻¹ K ⁻¹)	Atomic or Molecular Weight (amu)
H ₂ (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	112.7	201.8	35.9	27.03
CN ⁻ (aq)	150.6	172.4	94.1		26.02
HCO ₂ ⁻ (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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E&R prob 4.20b HW3 #16

P4.20 If 3.059 g of ethanol, C₂H₅OH(l) is burned completely in a bomb calorimeter at 298.15 K, the heat produced is 90.447 kJ.

- Calculate $\Delta H_{\text{combustion}}^\circ$ for ethanol at 298.15 K.
- Calculate ΔH_f° of ethanol at 298.15 K.

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TABLE 4.1 (CONTINUED)

Substance	ΔH_f° (kJ mol ⁻¹)	ΔG_f° (kJ mol ⁻¹)	S° (J mol ⁻¹ K ⁻¹)	$C_{p,m}$ (J mol ⁻¹ K ⁻¹)	Atomic or Molecular Weight (amu)
H ₂ (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	112.7	201.8	35.9	27.03
CN ⁻ (aq)	150.6	172.4	94.1		26.02
HCO ₂ ⁻ (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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TABLE 4.2 THERMODYNAMIC DATA FOR SELECTED ORGANIC COMPOUNDS AT 298.15 K

Substance	Formula	Molecular Weight	ΔH_f° (kJ mol ⁻¹)	$\Delta H_{\text{combustion}}^\circ$ (kJ mol ⁻¹)	ΔG_f° (kJ mol ⁻¹)	S° (J mol ⁻¹ K ⁻¹)	$C_{p,m}$ (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	-3208	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	58.08	-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 ₅ O	46.07	-277.6	-1367	-174.8	160.7	112.3
Ethanol(g)	C ₂ H ₅ 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	44.1
Formaldehyde(g)	CH ₂ O	30.03	-108.6	-571	-102.5	218.8	35.4

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

↑

\bar{H}_f° at 298K in kJ/mol

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

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Raff Table 3.2 bond enthalpies

3.3 Bond Enthalpies 135

Table 3.2 Average bond enthalpies in kJ mol ⁻¹										
	H	C	N	O	F	Cl	Br	I	S	P
H	436									
C	415	348(a) 612(d) 838(e) 518(a*)								
N	391	292(a) 616(d) 890(e)	361(a)							
O	463	355(a) 734(d)	166	145(a)						
F	565	484	270	185	156					
Cl	431	323	200	209	254	243				
Br	366	276	219	219	219	193				
I	299	238	210	178	151					
S	353	259	696	250	212		265			
P	322							201		

(a) single bond, (d) double bond, (e) triple bond, (a*) aromatic bond
 Data: Pilling, L. General Chemistry, 3d, ed., Freeman, San Francisco, 1970; Atlas, P. Physical Chemistry, 5th, ed., Freeman, New York, 1994. Where the data differ, averages are taken.

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