Chemistry 163B Winter 2013
Lectures 6-7 Thermochemistry

Chemistry 163B

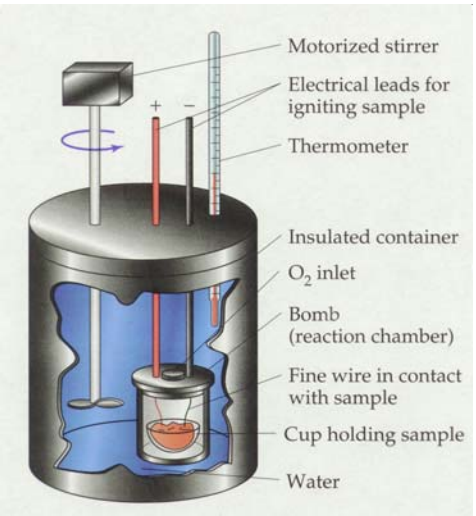
Thermochemistry

Chapter 4 Engel & Reid

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

$$\Delta U_V = q_V$$

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



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

$$\Delta U_V = q_V$$

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

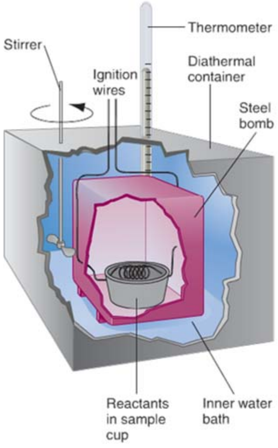


FIGURE 4.3

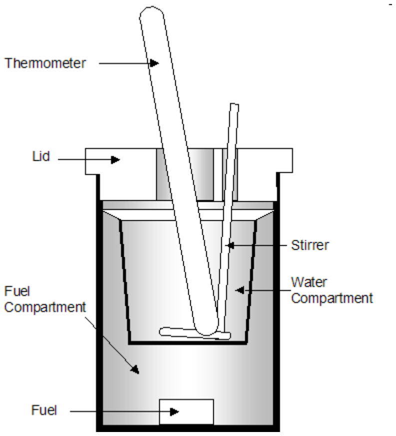
FIGURE 4.3
Schematic diagram of a bomb calorimeter. The liquid or solid reactant is placed in a cup suspended in the thick-walled steel bomb, which is filled with O_2 gas. The vessel is immersed in an inner water bath, and its temperature is monitored. The diathermal container is immersed in an outer 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.

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.

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

$$\Delta H_P = q_P$$

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



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

$$\boxed{\begin{array}{c}\Delta H_P = q_P \\ \\ \Delta H = H_{products} - H_{reactants}\end{array}}$$

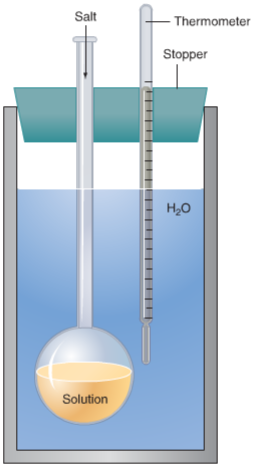


FIGURE 4.4
Schematic diagram of a constant pressure calorimeter suitable for measuring the enthalpy of solution of a salt in water.

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

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

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

SiO_2 (α quartz) → SiO_2 (β quartz) $\Delta H_{848} = -907$ kJ

$NaCl(s) + H_2O(\ell) \rightarrow Na^+(aq) + Cl^-(aq)$ $\Delta H_{298} = +3.9$ kJ

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

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

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Hess's Law

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

ΔH State Function ⇨ Hess's Law

$$\begin{tikzcd}
O_2(g) + C\,(gr) \arrow[rr, "I", "\Delta H_I=?"'] \arrow[dr, "II"'] & & C(dia) + O_2(g) \\
& CO_2(g) \arrow[ur, "III"'] &
\end{tikzcd}$$

$\Delta H_{II}=\Delta H_{combustion}(gr)$

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

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

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

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

factors affecting $\Delta H_{reaction}$

- 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

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

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

total enthalpy of reactants

molar enthalpy of reactant i

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

number of moles of i in stoichiometry

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

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

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

$\nu_i = \ n_i$ ***if*** i ***is product species***

$\nu_i = -n_i$ ***if*** i ***is reactant species***

$\Delta H_{reaction}$ 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

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

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

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

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

E&R eqn 4.25

standard states and enthalpies of formation (done on board)

standard state

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

often T is assumed 298K for standard state

$$\Delta H^{\circ}_{298}$$

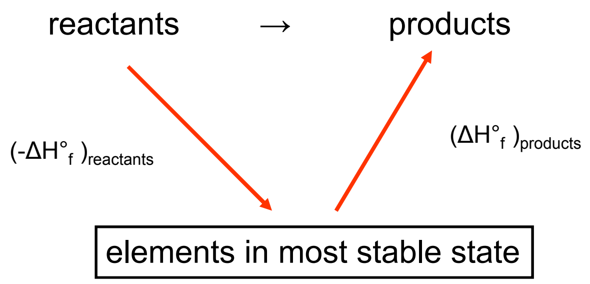
define standard states ➡

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

molar enthalpy of formation

define enthalpy of formation ➡

ΔH°_{rxn} from H°_{f}



$$(\Delta H^{\circ})_{rxn} = \sum_{i} \upsilon_i (\bar{H}^{0}_{f})_i$$

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

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

- ✓ 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

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temperature dependence of H of substance at constant P

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

change in enthalpy of substance $T_1 \longrightarrow T_2$

for a given reactant or product at constant P

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

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

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

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

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

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

vs

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

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

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

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

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

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

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

$$\boxed{\begin{aligned}&\Delta H_{reaction}(T_2) = \Delta H_{reaction}(T_1) + \int_{T_1}^{T_2} \Delta C_P dT \\ &\textit{where} \quad \Delta C_P = \sum_i \nu_i (\bar{C}_P)_i = \text{"}(C_P)_{products} - (C_P)_{reactants}\text{"}\end{aligned}}$$

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example problems : ΔH from H_f and ΔH T=298K ⟶ 398K

$$3C_2H_2\,(g) \longrightarrow C_6H_6\,(\ell) \qquad \text{calc } \Delta H^o_{298}$$

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

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

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

$$3C_2H_2\,(g) \longrightarrow C_6H_6\,(\ell) \qquad \text{calc } \Delta H^o_{398}$$

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

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

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

C_P independent of T

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

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

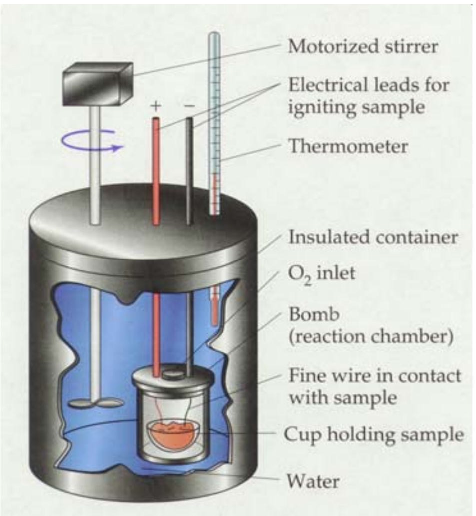
- ✓ Calculate $\Delta H_{reaction}$
  Hess's Law, standard heats of formation
- ✓ $\Delta H_{reaction}$ vs $\Delta U_{reaction}$
- ✓ Temperature (and pressure) dependence of $\Delta H_{reaction}$
- Calorimetry
- Heats of solution
- $\Delta H_{reaction}$ from bond enthalpies

MIDTERM 1

heats of reactions (constant volume)

$$\Delta U_V = q_V$$

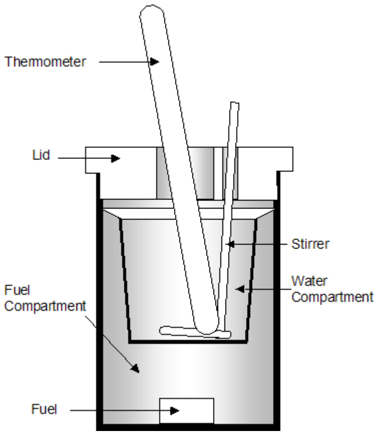
$$\Delta U = U_{products} - U_{reactants}$$



heats of reactions (constant pressure)

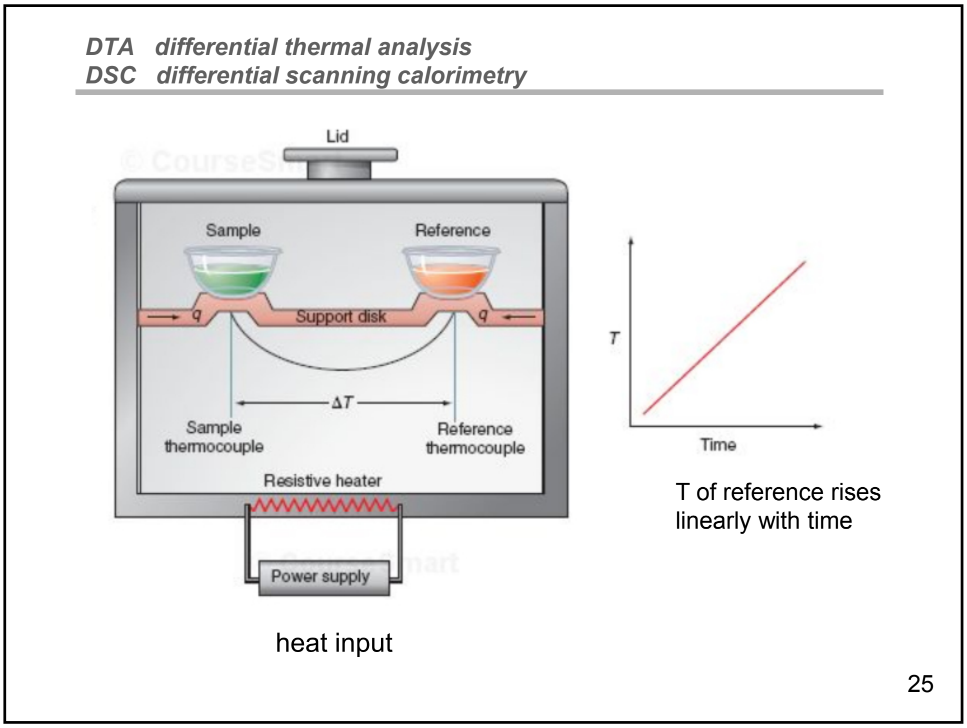
$$\Delta H_P = q_P$$

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



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

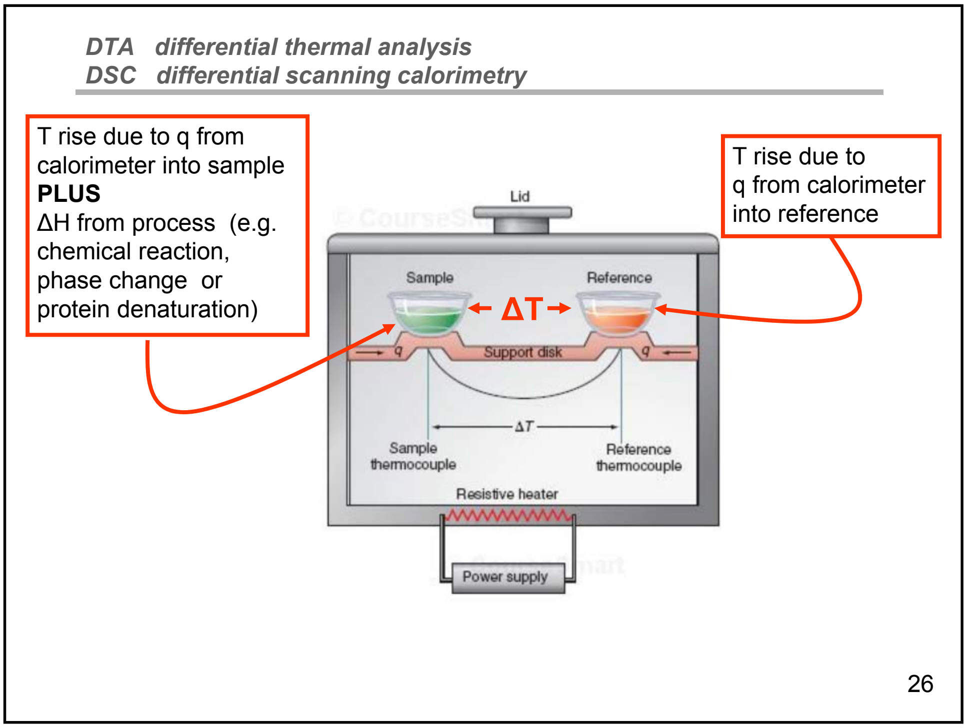
useful for small samples (often biological)



DTA differential thermal analysis
DSC differential scanning calorimetry

T of reference rises linearly with time

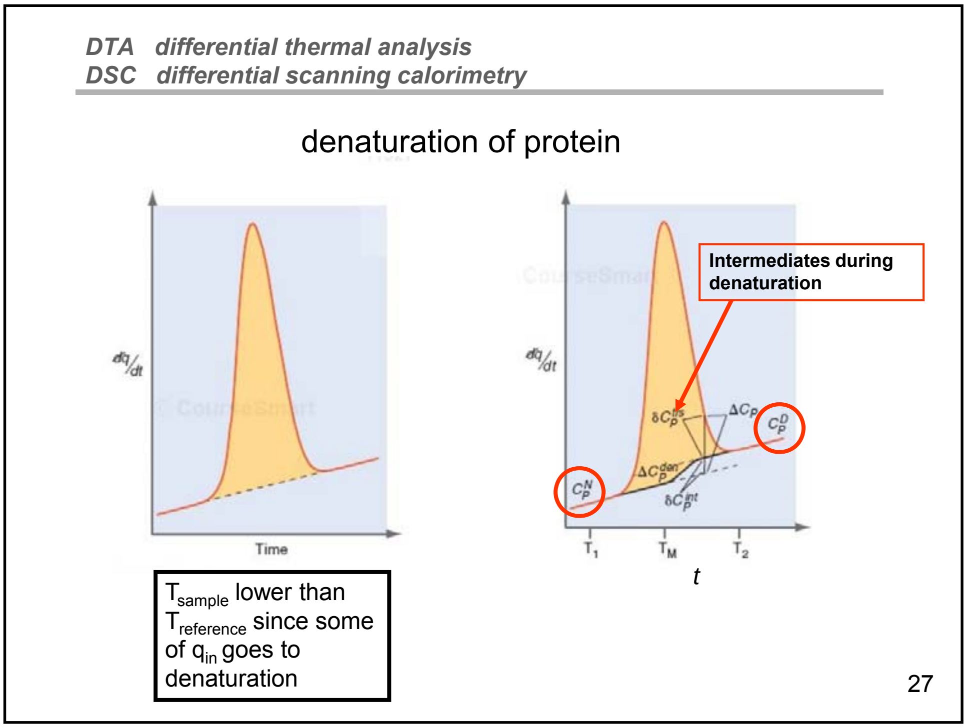
heat input



DTA differential thermal analysis
DSC differential scanning calorimetry

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



DTA differential thermal analysis
DSC differential scanning calorimetry

denaturation of protein

Intermediates during denaturation

T_{sample} lower than $T_{reference}$ since some of q_{in} goes to denaturation

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 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

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 $\bar{H}_f^0(\mathrm{H}^+(aq,\ 1M)_{ideal})=0$

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

heats of formation of ions (heat of solutions)

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

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

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

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

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

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

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

NOW

heats of formation of ions (heat of solutions)

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

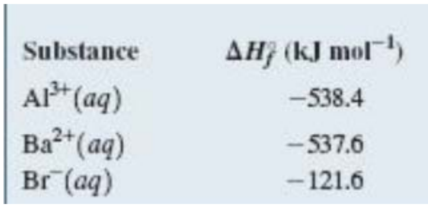
$$NaCl(s) \xrightarrow{H_2O} Na^+(aq,\ 1M)_{ideal} + Cl^-(aq,\ 1M)_{ideal}$$

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

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

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

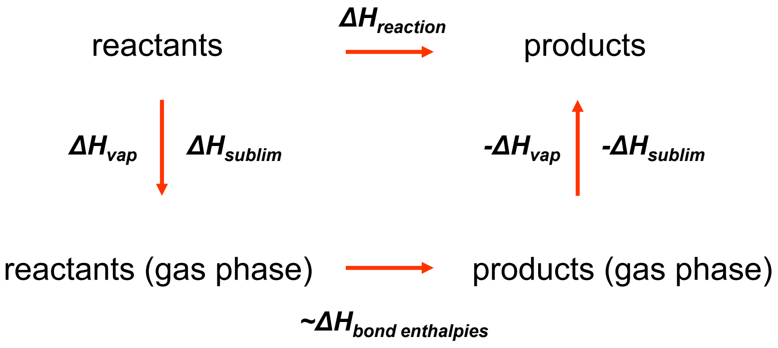
$$\bar{H}_f^0(Na^+(aq)) = -240.1\ kJ\ mol^{-1}$$



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

etc.

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

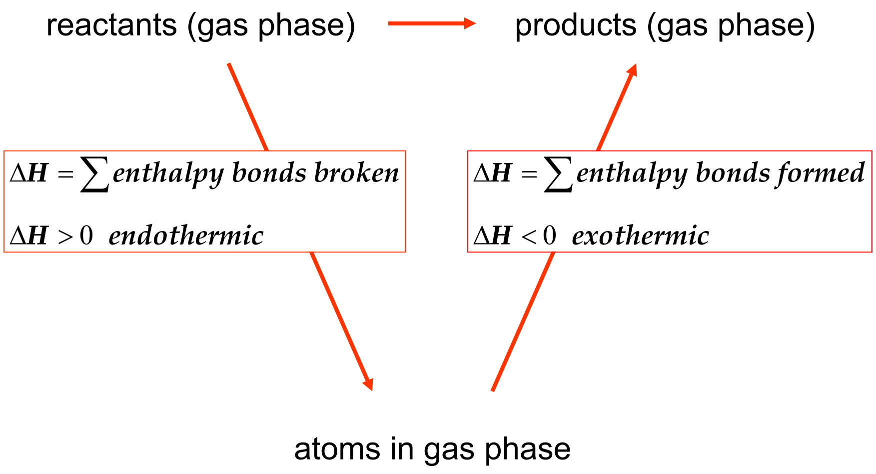


$\Delta H_{reaction}$ from bond enthalpies

- 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** $\Delta H_{reaction}$

$\Delta H_{reaction}$ from bond enthalpies



reactants (gas phase) → products (gas phase)

$\Delta H = \sum enthalpy\ bonds\ broken$

$\Delta H > 0\ \ endothermic$

$\Delta H = \sum enthalpy\ bonds\ formed$

$\Delta H < 0\ \ exothermic$

atoms in gas phase

$\Delta H_{reaction}$ from bond enthalpies

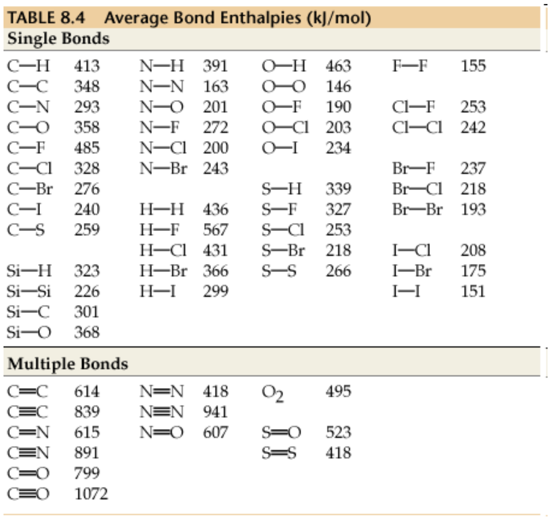


TABLE 8.4 Average Bond Enthalpies (kJ/mol)

Single Bonds

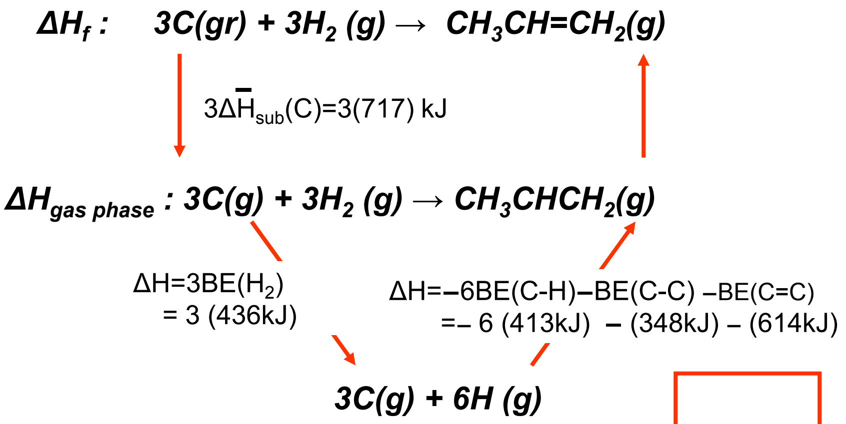
C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C—N	293	N—O	201	O—F	190	Cl—F	253
C—O	358	N—F	272	O—Cl	203	Cl—Cl	242
C—F	485	N—Cl	200	O—I	234		
C—Cl	328	N—Br	243			Br—F	237
C—Br	276			S—H	339	Br—Cl	218
C—I	240	H—H	436	S—F	327	Br—Br	193
C—S	259	H—F	567	S—Cl	253		
		H—Cl	431	S—Br	218	I—Cl	208
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 $CH_3CH=CH_2(g)$



ΔH_f : $3C(gr) + 3H_2(g) \rightarrow CH_3CH=CH_2(g)$

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

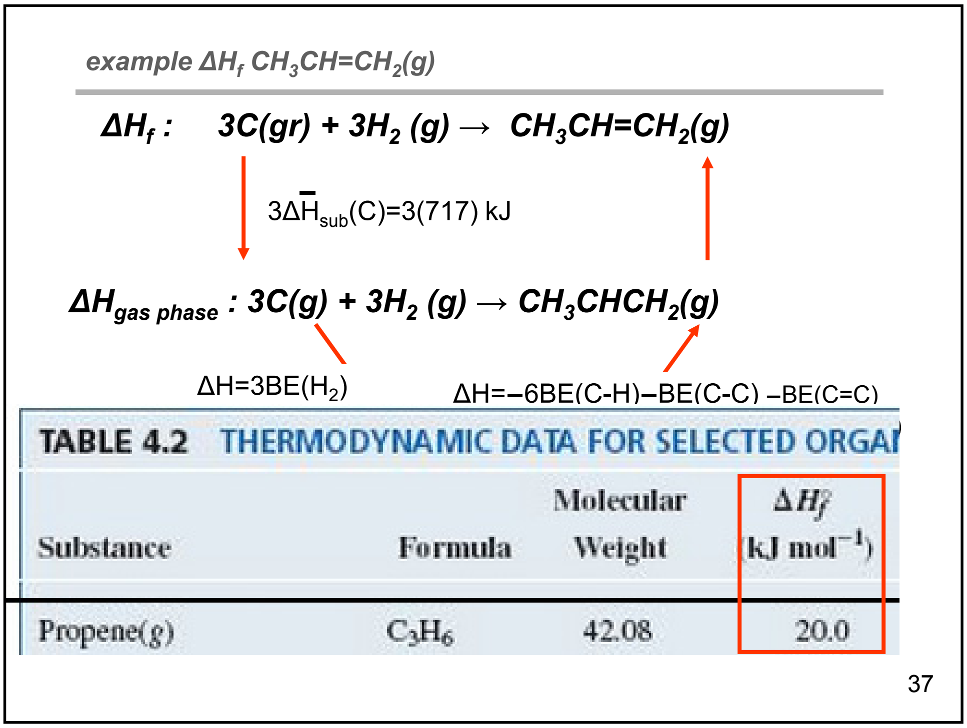
$\Delta H_{gas\ phase}$: $3C(g) + 3H_2(g) \rightarrow CH_3CHCH_2(g)$

$\Delta H=3BE(H_2)$
$= 3\ (436kJ)$

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

$3C(g) + 6H(g)$

$$\boxed{\Delta H_f = (3\times717 + 3\times436 - 6\times413 - 348 - 614)\,\text{kJ} = \mathbf{19}\ \text{kJ}}$$



example ΔH_f $CH_3CH{=}CH_2(g)$

ΔH_f : $3C(gr) + 3H_2(g) \rightarrow CH_3CH{=}CH_2(g)$

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

$\Delta H_{gas\ phase}$: $3C(g) + 3H_2(g) \rightarrow CH_3CHCH_2(g)$

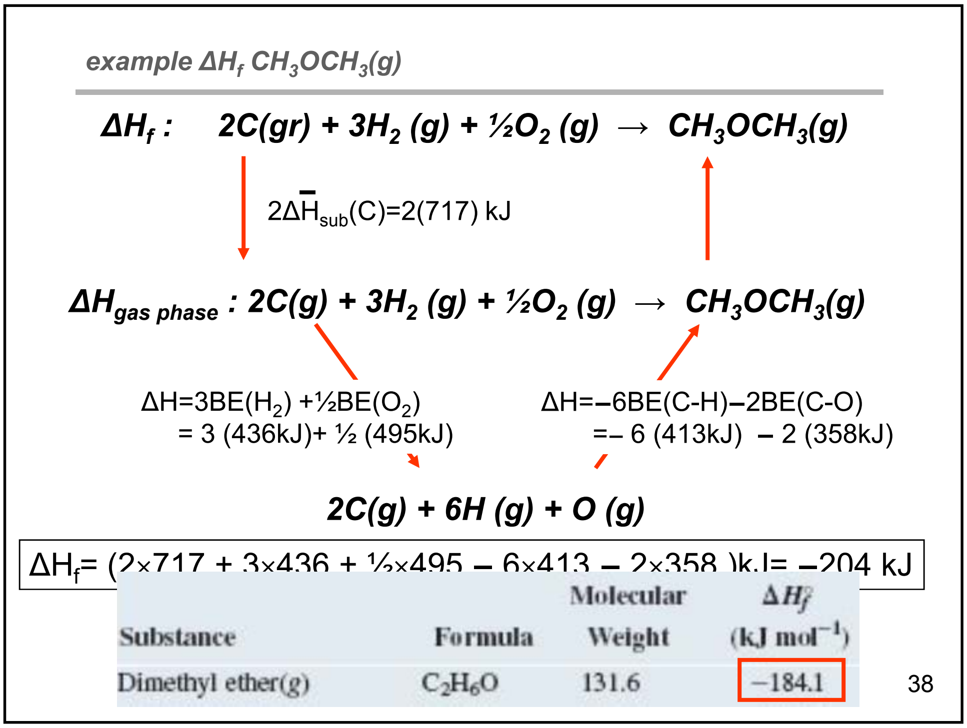
$\Delta H = 3BE(H_2)$

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

TABLE 4.2 THERMODYNAMIC DATA FOR SELECTED ORGA

Substance	Formula	Molecular Weight	ΔH_f° (kJ mol^{-1})
Propene(*g*)	C_3H_6	42.08	20.0

37



example ΔH_f $CH_3OCH_3(g)$

ΔH_f : $2C(gr) + 3H_2(g) + ½O_2(g) \rightarrow CH_3OCH_3(g)$

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

$\Delta H_{gas\ phase}$: $2C(g) + 3H_2(g) + ½O_2(g) \rightarrow CH_3OCH_3(g)$

$\Delta H = 3BE(H_2) + ½BE(O_2)$
$= 3\ (436kJ) + ½\ (495kJ)$

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

$2C(g) + 6H(g) + O(g)$

$\Delta H_f = (2\times717 + 3\times436 + ½\times495 - 6\times413 - 2\times358)\text{kJ} = -204\text{ kJ}$

Substance	Formula	Molecular Weight	ΔH_f° (kJ mol^{-1})
Dimethyl ether(*g*)	C_2H_6O	131.6	−184.1

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bond enthalpy vs bond energy

- 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. 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)

table 4.3 E&R

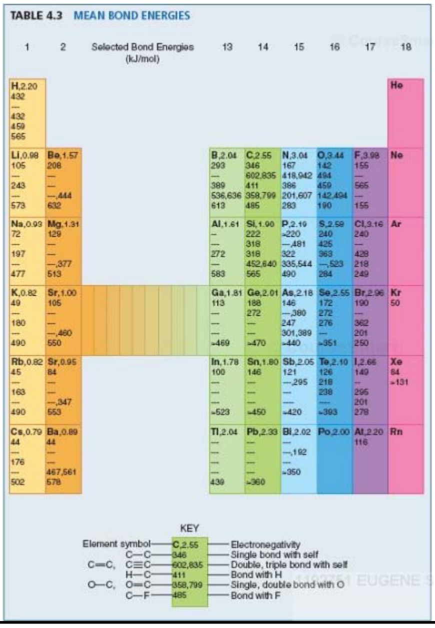


TABLE 4.3 MEAN BOND ENERGIES

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

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

- ✓ 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

E&R prob 4.20b HW3 #16

P4.20 If 3.365 g of ethanol $C_2H_5OH(l)$ is burned completely in a bomb calorimeter at 298.15 K, the heat produced is 99.472 kJ.

a. Calculate $\Delta H^\circ_{combustion}$ for ethanol at 298.15 K.

b. Calculate ΔH°_f of ethanol at 298.15 K.

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

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

$$a.\ q_{??} \Rightarrow \Delta\bar{U} \Rightarrow \Delta\bar{H}^0_{combustion}$$

(assume pure liquids,
gases 1 bar partial pressure)

E&R prob 4.20b HW3 #16 (cont)

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

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

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

SOLVE FOR H_f(EtOH)

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

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

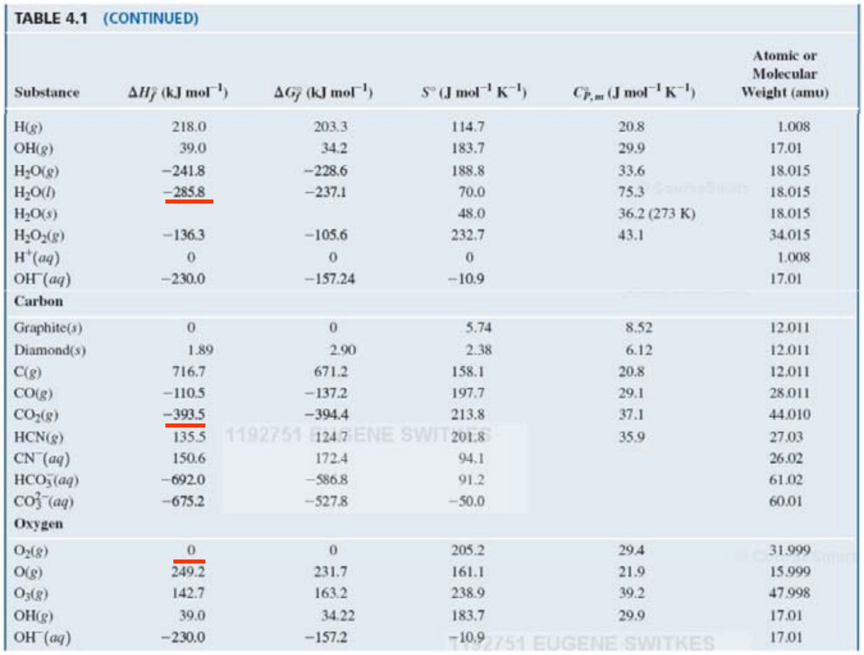
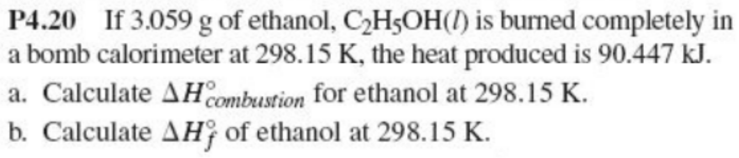


TABLE 4.1 (CONTINUED)

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
$H_2O(g)$	−241.8	−228.6	188.8	33.6	18.015
$H_2O(l)$	$\underline{-285.8}$	−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
$CO_2(g)$	$\underline{-393.5}$	−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					
$O_2(g)$	$\underline{0}$	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

E&R prob 4.20b HW3 #16



P4.20 If 3.059 g of ethanol, $C_2H_5OH(l)$ is burned completely in a bomb calorimeter at 298.15 K, the heat produced is 90.447 kJ.

a. Calculate $\Delta H^\circ_{combustion}$ for ethanol at 298.15 K.

b. Calculate ΔH_f° of ethanol at 298.15 K.

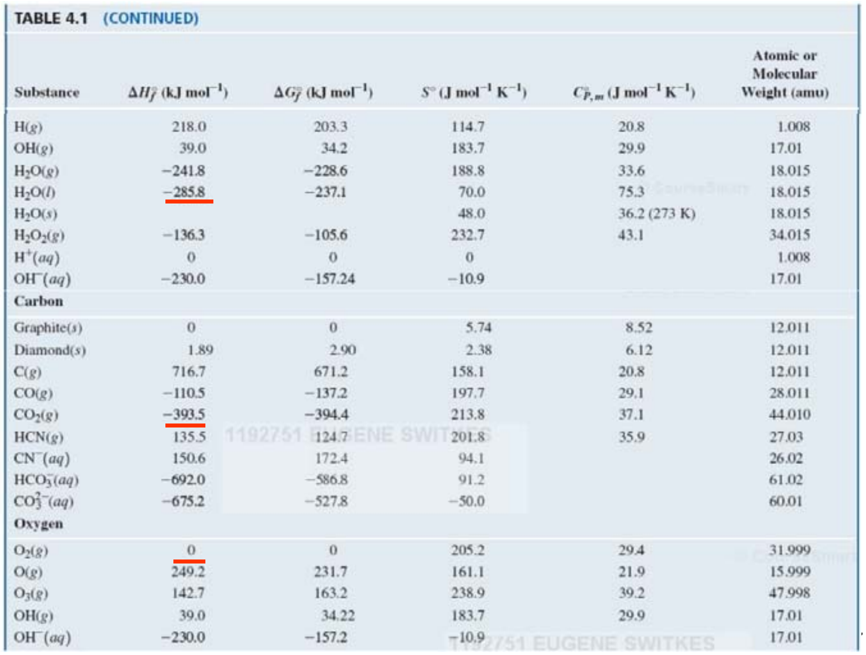


TABLE 4.1 (CONTINUED)

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

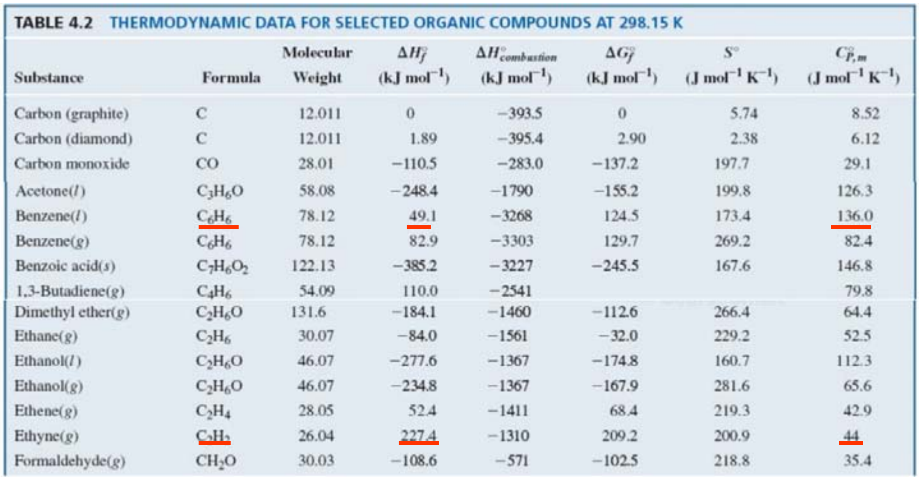


TABLE 4.2 THERMODYNAMIC DATA FOR SELECTED ORGANIC COMPOUNDS AT 298.15 K

Substance	Formula	Molecular Weight	ΔH_f° (kJ mol^{-1})	$\Delta H^\circ_{combustion}$ (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_3H_6O	58.08	−248.4	−1790	−155.2	199.8	126.3
Benzene(*l*)	C_6H_6	78.12	49.1	−3268	124.5	173.4	136.0
Benzene(*g*)	C_6H_6	78.12	82.9	−3303	129.7	269.2	82.4
Benzoic acid(*s*)	$C_7H_6O_2$	122.13	−385.2	−3227	−245.5	167.6	146.8
1,3-Butadiene(*g*)	C_4H_6	54.09	110.0	−2541			79.8
Dimethyl ether(*g*)	C_2H_6O	131.6	−184.1	−1460	−112.6	266.4	64.4
Ethane(*g*)	C_2H_6	30.07	−84.0	−1561	−32.0	229.2	52.5
Ethanol(*l*)	C_2H_6O	46.07	−277.6	−1367	−174.8	160.7	112.3
Ethanol(*g*)	C_2H_6O	46.07	−234.8	−1367	−167.9	281.6	65.6
Ethene(*g*)	C_2H_4	28.05	52.4	−1411	68.4	219.3	42.9
Ethyne(*g*)	C_2H_2	26.04	227.4	−1310	209.2	200.9	44
Formaldehyde(*g*)	CH_2O	30.03	−108.6	−571	−102.5	218.8	35.4

standard states and standard heats of formation

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

$\bar{H}_f^0$ *at 298K in kJ/mol*

$C(gr)=0 \quad O_2(g)=0 \quad C(dia)=1.89 \quad H_2O(g)=-241.8 \quad H_2O(\ell)=-285.8$

$F_2(g)=0 \quad Cl_2(g)=0 \quad I_2(g)=62.4 \quad I_2(s)=0$