

Chemistry 163B Winter 2020

Lectures 6-7 Thermochemistry

Chemistry 163B
Lectures 6-7
Thermochemistry
Chapter 4 Engel & Reid

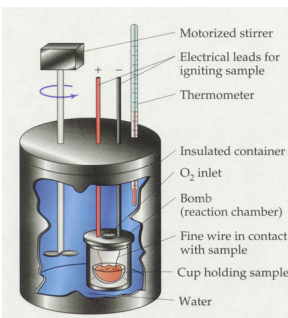
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heats of reactions (constant volume; 'bomb' calorimeter)

$$\Delta U_V = q_V$$

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



2

2

heats of reactions (constant volume; fig 4.3 E&R_{4th})(4.3)3rd

$$\Delta U_V = q_V$$

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

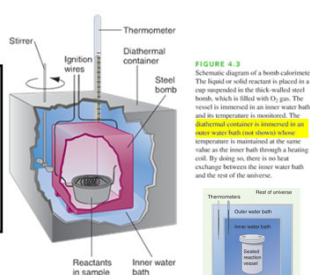


FIGURE 4.3 Schematic diagram of a bomb calorimeter. The liquid or solid reactant is placed in a cup suspended in the thick-walled steel bomb which is filled with O₂ gas. The vessel is immersed in an inner water bath, and the temperature is measured. The insulated container is immersed in an outer water bath to ensure thermal equilibrium 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.

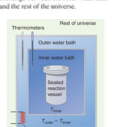


FIGURE 4.3 An isolated composite system is created in which the surroundings are the universe. All masses are treated as closed. The walls surrounding the inner water bath are rigid.

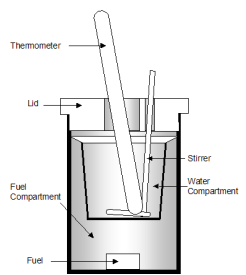
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3

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

$$\Delta H_P = q_P$$

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



4

4

heats of reactions (constant pressure; fig 4.4 E&R_{4th})(4.4)3rd

$$\Delta H_P = q_P$$

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

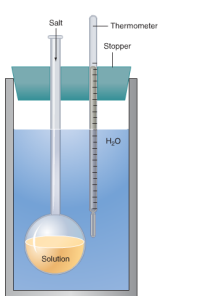


FIGURE 4.4 Schematic diagram of a constant pressure calorimeter suitable for measuring the enthalpy of solution of a salt in water.

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

$$\text{C}(\text{gr}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \quad \Delta H_{298} = -393 \text{ kJ}$$

$$\text{ATP} + \text{H}_2\text{O} \rightarrow \text{ADP} + \text{H}_3\text{PO}_4 \quad \Delta H_{298} \approx -20.5 \text{ kJ}$$

$$\text{SiO}_2 (\alpha \text{ quartz}) \rightarrow \text{SiO}_2 (\beta \text{ quartz}) \quad \Delta H_{848} = -907 \text{ kJ}$$

$$\text{NaCl}(\text{s}) + \text{H}_2\text{O} (\ell) \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \quad \Delta H_{298} = +3.9 \text{ kJ}$$

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Lectures 6-7 Thermochemistry

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

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

----- MIDTERM 1 ----- 7

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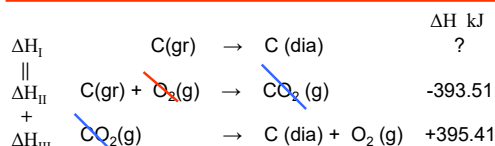
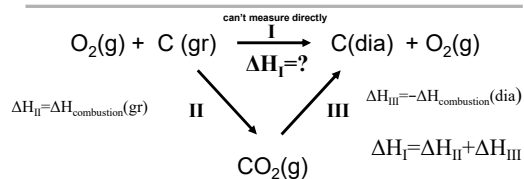
Hess's Law

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

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ΔH State Function \Rightarrow Hess's Law



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

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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



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

total enthalpy of reactants

molar enthalpy of reactant i

number of moles of i in stoichiometry

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

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

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

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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:

i) PV and ΔPV is small for solids and liquids

ii) 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, 4th, eqn 4.23 ??

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

standard state

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

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

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

$\Delta \bar{H}^\circ_{298}$

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

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 P4.33b)

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Hess's Law, standard heats of formation
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- Temperature (and pressure) dependence of $\Delta H_{\text{reaction}}$
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- $\Delta H_{\text{reaction}}$ from bond enthalpies

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

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temperature dependence of H of substance at constant P

change in enthalpy of substance $T_1 \rightarrow T_2$

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

for a given reactant or product at constant P

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

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

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

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

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

$$\Delta H_{\text{reaction}} = \sum_i \nu_i \bar{H}_i \quad (\Delta C_p)_{\text{reaction}} = \sum_i \nu_i (\bar{C}_p)_i$$

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

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

vs

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

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

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

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

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

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example problems : ΔH from H_f° and ΔH $T=298\text{K} \Rightarrow 398\text{K}$

$3\text{C}_2\text{H}_2(\text{g}) \rightarrow \text{C}_6\text{H}_6(\text{l})$ 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	$(\text{J K}^{-1} \text{ mol}^{-1})$
$\Delta \bar{C}_p$	$-3(44.0)$	$+ 1(136.0)$	$= 4.0 (\text{J K}^{-1})$
$(\Delta H^\circ)_{398}$	$= (\Delta H^\circ)_{298} + \int_{298}^{398} \Delta C_p dT = (\Delta H^\circ)_{298} + \Delta C_p \Delta T$ C_p independent of T		
$(\Delta H^\circ)_{398}$	$= -633.1 \text{ kJ} + (4.0 \times 10^{-3} \text{ kJ K}^{-1})(100\text{K}) = -632.7 \text{ kJ}$		

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

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Hess's Law, standard heats of formation
- ✓ • $\Delta H_{\text{reaction}}$ vs $\Delta U_{\text{reaction}}$
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- Heats of solution
- $\Delta H_{\text{reaction}}$ from bond enthalpies

MIDTERM 1

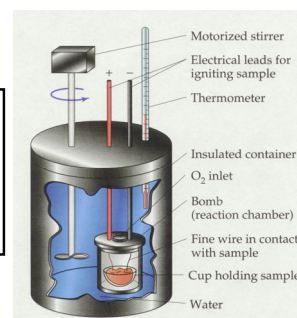
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heats of reactions (constant volume)

$$\Delta U_V = q_V$$

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



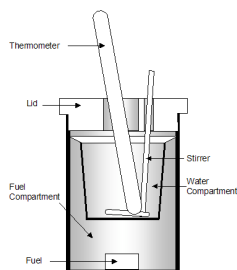
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heats of reactions (constant pressure)

$$\Delta H_P = q_P$$

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



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

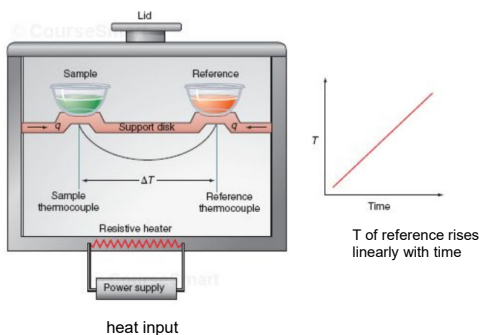


useful for small samples (often biological)

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DTA differential thermal analysis DSC differential scanning calorimetry



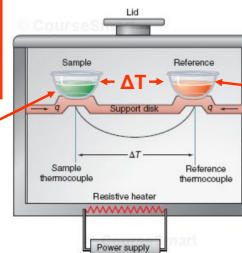
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DTA differential thermal analysis DSC differential scanning calorimetry

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

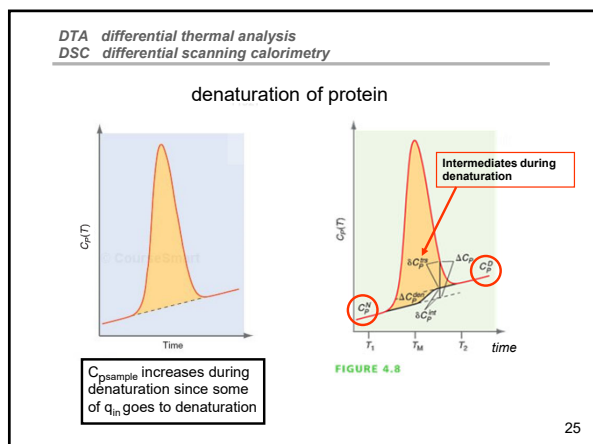


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how H and ΔH change with pressure (don't FRET now)

will prove later:

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

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

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

Will show later:

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

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heats of formation of ions (heat of solutions), (Example 4.4 p 73)_{3rd}

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^+

another importance: HW3 #21 E&R_{4th} P4.5d
21. P4.5 Calculate $\Delta_r H^\circ$ and $\Delta_r U^\circ$ at 298.15 K for the following reactions:
d. $2\text{NaOH}(\text{aq}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{Na}_2\text{SO}_4(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$

Assume complete dissociation of NaOH , H_2SO_4 , and Na_2SO_4 .

$$\Delta H_{\text{reaction}} = -2\Delta \bar{H}_f^0(\text{Na}^+) - 2\Delta \bar{H}_f^0(\text{OH}^-) - 2\Delta \bar{H}_f^0(\text{H}^+) - \Delta \bar{H}_f^0(\text{SO}_4^{2-}) + 2\Delta \bar{H}_f^0(\text{Na}^+) + \Delta \bar{H}_f^0(\text{SO}_4^{2-}) + 2\Delta \bar{H}_f^0(\text{H}_2\text{O})$$

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heats of formation of ions (heat of solutions)

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

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

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

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

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

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

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

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heats of formation of ions (heat of solutions)

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

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

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

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

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

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

Substance	$\Delta \bar{H}_f^0$ (kJ mol ⁻¹)	etc.
$\text{Al}^{3+}(\text{aq})$	-538.4	
$\text{Ba}^{2+}(\text{aq})$	-537.6	
$\text{Br}^-(\text{aq})$	-121.6	

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$\Delta H_{\text{reaction}}$ from bond enthalpies (p. 92)_{ER4th} [p. 69]_{ER3rd}

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

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

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

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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) \rightarrow products (gas phase)

$\Delta H = \sum \text{enthalpy bonds broken}$
 $\Delta H > 0$ endothermic

$\Delta H = \sum \text{enthalpy bonds formed}$
 $\Delta H < 0$ 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
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	S-H	339
C-I	240	H-H	436
C-S	259	H-F	567
Si-H	323	H-Cl	431
Si-Si	226	H-Br	366
Si-C	301	H-I	299
Si-O	368	S-S	266
		I-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>

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

$\Delta H_f: 3\text{C}(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow \text{CH}_3\text{CH}=\text{CH}_2(\text{g})$

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

$\Delta H_{\text{gas phase}}: 3\text{C}(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow \text{CH}_3\text{CHCH}_2(\text{g})$

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

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

$3\text{C}(\text{g}) + 6\text{H}(\text{g})$

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

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

$\Delta H_f: 3\text{C}(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow \text{CH}_3\text{CH}=\text{CH}_2(\text{g})$

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

$\Delta H_{\text{gas phase}}: 3\text{C}(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow \text{CH}_3\text{CHCH}_2(\text{g})$

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

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

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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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 $\Delta H = \Delta U + \Delta n_{\text{gas}}RT$ 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)

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table 4.3 E&R

TABLE 4.3 MEAN BOND ENERGIES

1	2	3	4	5	6	7	8
Li 2.00							He
Na 0.98							
K 0.81							
Rb 0.72							
Cs 0.66							
Ca 1.04	1.07						He
Sc 1.04							
Ti 1.04							
V 1.04							
Cr 1.04							
Mn 1.04							
Fe 1.04							
Co 1.04							
Ni 1.04							
Cu 1.04							
Zn 1.04							
Ga 1.04	1.04						Ar
Ge 1.04							
As 1.04							
Se 1.04							
Br 1.04							
Kr 1.04							
Rb 1.04							
Cs 1.04							
Ba 1.04							
La 1.04							
Ce 1.04							
Pr 1.04							
Nd 1.04							
Pm 1.04							
Sm 1.04							
Eu 1.04							
Gd 1.04							
Tb 1.04							
Dy 1.04							
Ho 1.04							
Er 1.04							
Tm 1.04							
Yb 1.04							
Lu 1.04							
Hf 1.04							
Ta 1.04							
W 1.04							
Re 1.04							
Os 1.04							
Ir 1.04							
Pt 1.04							
Au 1.04							
Hg 1.04							
Tl 1.04							
Pb 1.04							
Bi 1.04							
Po 1.04							
At 1.04							
Rn 1.04							

KEY

- Element symbol
- Electronegativity
- C=C
- C≡C
- Single bond with H
- Double bond with H
- Triple bond with H
- Single, double bond with O
- C-F
- Bond with F

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

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Si-O	368		
O-H	463	I-F	155
O-O	146	Cl-F	253
O-F	190	Cl-Cl	242
O-Cl	203	Br-F	237
O-I	234	Br-Cl	218
S-F	327	Br-Br	193
S-Cl	253	I-Cl	208
S-Br	218	I-Br	175
S-S	266	I-I	151

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=O	799			S=S	418
C=O	1072				

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

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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 4th, prob 4.33 HW3 #16

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 $\Delta H_{\text{combustion}}^{\circ}$ 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: $\text{C}_2\text{H}_5\text{OH}(\ell) + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\ell)$

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

bomb calorimeter $\Rightarrow q_{\text{??}}$

$q_v = \Delta U \Rightarrow \Delta \bar{H}_{\text{combustion}}^{\circ}$
(assume pure liquids, gases 1 bar partial pressure)

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E&R prob 4.33b HW3 #16 (cont) using $\Delta H_{\text{comb}}^{\circ}$ from 4.33a

$\text{C}_2\text{H}_5\text{OH}(\ell) + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\ell)$

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

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

$\sum_i \nu_i (\Delta \bar{H}_f^{\circ})_i$ **SOLVE FOR $\Delta H_f^{\circ}(\text{EtOH})$**

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

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

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Chemistry 163B Winter 2020

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(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)	<u>-285.8</u>	-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)	<u>135.5</u>	119.275 ¹	124.7	201.8 ¹	35.9
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)	<u>249.2</u>	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_{4th} prob 4.33b HW3 #16

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 $\Delta H^\circ_{\text{combustion}}$ 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) !!]

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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(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)	<u>-285.8</u>	-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)	<u>135.5</u>	119.275 ¹	124.7	201.8 ¹	35.9
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)	<u>249.2</u>	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)	<u>C₆H₆</u>	78.12	49.1	-3208	124.5	173.4	136.0
Benzene(g)	<u>C₆H₆</u>	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 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)	<u>C₂H₂</u>	26.04	<u>227.4</u>	-1310	209.2	200.9	<u>44</u>
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 (molar) [-1m (molal)]

↑

standard molar heat of formation (\bar{H}_f° or $\Delta \bar{H}_f^\circ$):
 ($\Delta H_{\text{reaction}}^\circ$) 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)

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

C(gr)=0 O₂(g)=0 C(dia)=1.89 H₂O(g)=-241.8 H₂O(l)=-285.8
 F₂(g)=0 Cl₂(g)=0 I₂(g)=62.4 I₂(s)=0

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