Tutorial 7

HEATS OF REACTION

In a chemical reaction bonds are broken in the reactants and new bonds formed in the products. Energy is required to break bonds and energy is released when bonds are formed. The energy associated with a chemical reaction depends on the number and type of bonds broken and/or formed.

Every chemical species has a certain amount of "heat content," or enthalpy, H, which cannot be measured. However, differences in enthalpy can be measured. The net energy change for a reaction performed at constant pressure is the enthalpy change for the reaction. This enthalpy change, ΔH, has units kJ/mol and is defined:

(1) $\Delta H = H(products) - H(reactants)$

If energy is given off during a reaction, such as in the burning of a fuel, the products have less heat content than the reactants and ΔH will have a negative value; the reaction is said to be exothermic. If energy is consumed during a reaction, ΔH will have a positive value; the reaction is said to be endothermic.
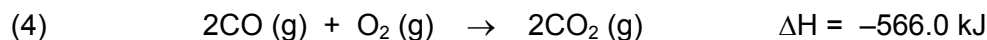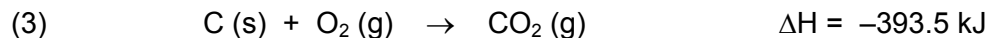
The enthalpy change for a chemical change is independent of the method or path by which the change is carried out as long as the initial and final substances are brought to the same temperature. This observation, known as HESS'S LAW, has important practical utility.

Thermochemical equations may be treated as algebraic equations: they may be written in the reverse direction with a change in the sign of ΔH – even though the reverse reaction may not actually occur; they may be added and subtracted algebraically; the equation and associated ΔH value may be multiplied or divided by factors. Hess's Law allows the calculation of enthalpy changes that would be difficult or impossible to determine directly, i.e. by experiment.

The enthalpy change for the reaction:

(2) $2C\ (s)\ +\ O_2\ (g)\ \rightarrow\ 2CO\ (g)$
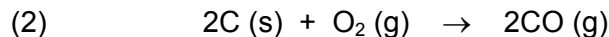
cannot be determined directly because carbon dioxide will also form. However, ΔH can be measured for:

(3) $C\ (s)\ +\ O_2\ (g)\ \rightarrow\ CO_2\ (g)$ $\Delta H = -393.5$ kJ

(4) $2CO\ (g)\ +\ O_2\ (g)\ \rightarrow\ 2CO_2\ (g)$ $\Delta H = -566.0$ kJ

Multiplying equation (3) by 2 gives equation (5), and reversing equation (4) gives equation (6):

(5) $2C$ (s) $+ 2O_2$ (g) $\rightarrow$ $2CO_2$ (g) $\Delta H = -787.0$ kJ

(6) $2CO_2$ (g) $\rightarrow$ $2CO$ (g) $+ O_2$ (g) $\Delta H = +566.0$ kJ
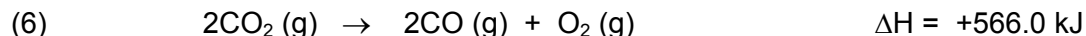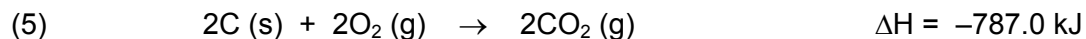
Adding equations (5) and (6) gives the desired information:

(2) $2C$ (s) $+ O_2$ (g) $\rightarrow$ $2CO$ (g) $\Delta H = -221.0$ kJ

For a reaction in which a compound is formed from the elements, the enthalpy change is called the heat of formation, ΔH_f^o, for the compound. The superscript "o" indicates standard conditions of one atmosphere pressure. Equation (2) and (3) are such reactions. Some others:

(7) S (s) $+ O_2$ (g) $\rightarrow$ SO_2 (g) $\Delta H = -296.9$ kJ

(8) Mg (s) $+ Cl_2$ (g) $\rightarrow$ $MgCl_2$ (s) $\Delta H = -641.8$ kJ
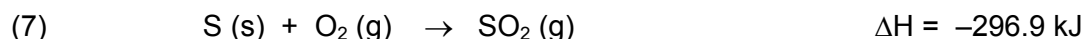
In reactions (2), (3), (7), and (8) ΔH for the reaction is ΔH_f^o for the compound. For the reaction:

(9) $2S$ (s) $+ 3O_2$ (g) $\rightarrow$ $2SO_3$ (g) $\Delta H = -790.4$ kJ
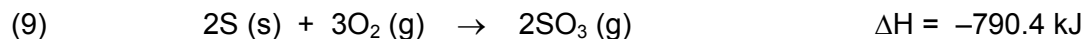
the heat of reaction is associated with the formation of two moles of SO_3. But heat of formation is per mole of compound, so ΔH_f^o for SO_3 is half of -790.4, or -395.2 kJ.

Extensive listings of heats of formation are available in handbooks. With these values of ΔH_f^o, you can calculate virtually any heat of reaction. The heat of a reaction is the sum of ΔH_f^o values for the products minus the sum of ΔH_f^o values for the reactants. Expressed as a formula:

(10) $\Delta H = \Sigma \ \Delta H_f^o$(products) $- \ \Sigma \ \Delta H_f^o$(reactants)

Heats of formation for several compounds are given on p T-56. A more extensive list can be found in Appendix C, pp 1019-1021, in your lecture text. Note that the phase of the compound is important when choosing a ΔH_f^o value for a calculation. By definition the heat of formation for a free element is zero.

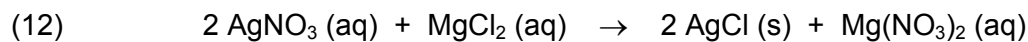## STANDARD HEATS OF FORMATION, ΔH_f^o, kJ/mole, at 25°C

AgCl (s)	−127.1	Ca(OH)$_2$ (s)	−986.1	K$_3$PO$_4$ (aq)	−2002.9
AgNO$_3$ (aq)	−100.7	Ca(OH)$_2$ (aq)	−1002.9	K$_2$SO$_4$ (aq)	−1409.2
AlCl$_3$ (s)	−695.4	HCl (g)	−92.3	MgCl$_2$ (aq)	−797.1
AlCl$_3$ (aq)	−1027.2	HCl (aq)	−167.4	Mg(NO$_3$)$_2$ (aq)	−875.1
Al(OH)$_3$ (s)	−1272.8	H$_2$O (g)	−241.8	NaCl (aq)	−407.1
Al$_2$(SO$_4$)$_3$ (aq)	−3753.5	H$_2$O (l)	−285.8	NaHCO$_3$ (s)	−947.7
BaCl$_2$ (aq)	−873.2	H$_3$PO$_4$ (aq)	−1294.1	NaNO$_3$ (aq)	−446.2
Ba(NO$_3$)$_2$ (aq)	−951.4	H$_2$SO$_4$ (l)	−814.0	NaOH (aq)	−469.4
BaSO$_4$ (s)	−1473.2	H$_2$SO$_4$ (aq)	−888.0	Na$_2$SO$_4$ (aq)	−1387.0
CaCl$_2$ (aq)	−877.8	KOH (aq)	−481.2	ZnCl$_2$ (aq)	−487.4

EXAMPLE: Using ΔH_f^o data calculate the heat of reaction for:

(11) $\qquad$ AgNO$_3$ (aq) + NaCl (aq) $\rightarrow$ AgCl (s) + NaNO$_3$ (aq)
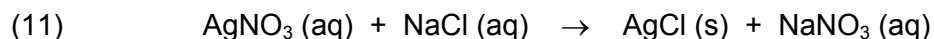
$\Delta H = [\Delta H_f^o \text{ AgCl (s)} + \Delta H_f^o \text{ NaNO}_3 \text{ (aq)}] - [\Delta H_f^o \text{ AgNO}_3 \text{ (aq)} + \Delta H_f^o \text{ NaCl (aq)}]$

$\quad = [(-127.0) + (-446.2)] - [(-100.7) + (-407.1)]$

$\quad = [-573.2] - [-507.8] = -573.2 + 507.8 = -65.4 \text{ kJ}$

EXAMPLE: Using ΔH_f^o data calculate the heat of reaction for:

(12) $\qquad$ 2 AgNO$_3$ (aq) + MgCl$_2$ (aq) $\rightarrow$ 2 AgCl (s) + Mg(NO$_3$)$_2$ (aq)

$\Delta H = [2 \Delta H_f^o \text{ AgCl (s)} + \Delta H_f^o \text{ Mg(NO}_3)_2 \text{ (aq)}] - [2 \Delta H_f^o \text{ AgNO}_3 \text{ (aq)} + \Delta H_f^o \text{ MgCl}_2 \text{ (aq)}]$

$\quad = [2(-127.0) + (-875.1)] - [2(-100.7) + (-797.1)]$

$\quad = [-1129.1] - [-998.5] = -1129.1 + 998.5 = -130.6 \text{ kJ}$

Note: the values of ΔH_f^o are multiplied by the stiochiometric coefficients from the balanced chemical equation.

(13) $2C$ (s) + O_2 (g) → $2CO$ (g)   ΔH = −221.0 kJ

(14) C (s) + O_2 (g) → CO_2 (g)   ΔH = −393.5 kJ

(15) $2H_2$ (g) + O_2 (g) → $2H_2O$ (g)   ΔH = −483.6 kJ

(16) $2H_2$ (g) + O_2 (g) → $2H_2O$ (l)   ΔH = −571.8 kJ

(17) CaO (s) + CO_2 (g) → $CaCO_3$ (s)   ΔH = −178.1 kJ

(18) $2Ca$ (s) + O_2 (g) → $2CaO$ (g)   ΔH = −1271.0 kJ
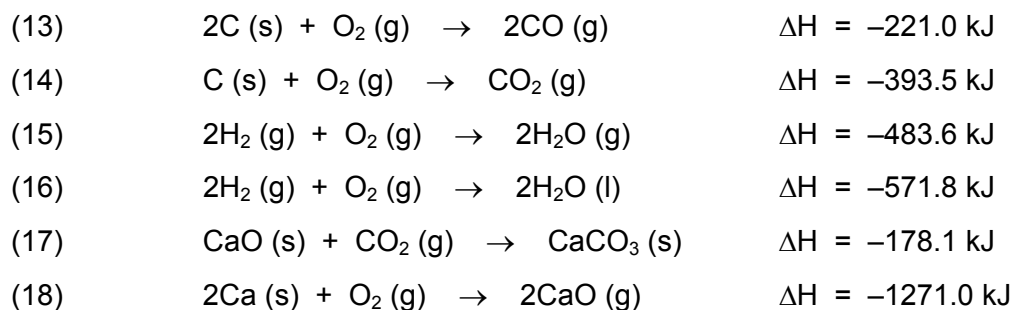
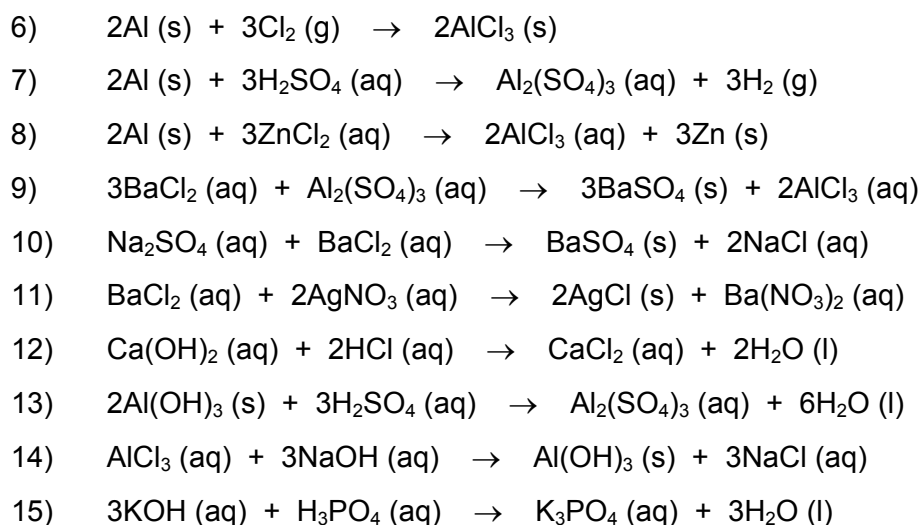Using Hess' Law with appropriate equations from (13)-(18), above, calculate ΔH for each of the following reactions:

1) H_2O (l) → H_2O (g)

2) C (s) + H_2O (g) → CO (g) + H_2 (g)

3) Ca (s) + H_2O (g) → CaO (s) + H_2 (g)

4) CO (g) + $1/2 O_2$ (g) → CO_2 (g)

5) $2Ca$ (s) + $2C$ (s) + $3O_2$ (g) → $2CaCO_3$ (s)
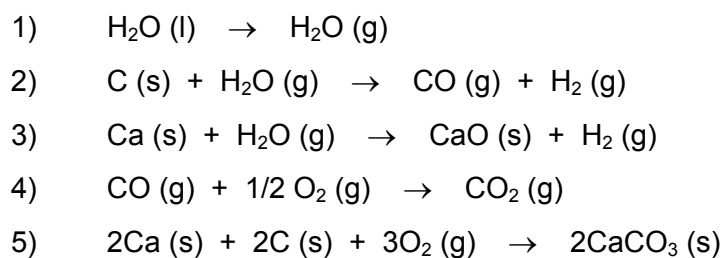
Using heats of formation values from page T-56 calculate ΔH for each of the following reactions:

6) $2Al$ (s) + $3Cl_2$ (g) → $2AlCl_3$ (s)

7) $2Al$ (s) + $3H_2SO_4$ (aq) → $Al_2(SO_4)_3$ (aq) + $3H_2$ (g)

8) $2Al$ (s) + $3ZnCl_2$ (aq) → $2AlCl_3$ (aq) + $3Zn$ (s)

9) $3BaCl_2$ (aq) + $Al_2(SO_4)_3$ (aq) → $3BaSO_4$ (s) + $2AlCl_3$ (aq)

10) Na_2SO_4 (aq) + $BaCl_2$ (aq) → $BaSO_4$ (s) + $2NaCl$ (aq)

11) $BaCl_2$ (aq) + $2AgNO_3$ (aq) → $2AgCl$ (s) + $Ba(NO_3)_2$ (aq)

12) $Ca(OH)_2$ (aq) + $2HCl$ (aq) → $CaCl_2$ (aq) + $2H_2O$ (l)

13) $2Al(OH)_3$ (s) + $3H_2SO_4$ (aq) → $Al_2(SO_4)_3$ (aq) + $6H_2O$ (l)

14) $AlCl_3$ (aq) + $3NaOH$ (aq) → $Al(OH)_3$ (s) + $3NaCl$ (aq)

15) $3KOH$ (aq) + H_3PO_4 (aq) → K_3PO_4 (aq) + $3H_2O$ (l)

Answers to Problems

1) +44.1 kJ   9) −76.9 kJ
2) +131.3 kJ   10) −19.2 kJ
3) −393.7 kJ   11) −130.8 kJ
4) −283.0 kJ   12) −111.7 kJ
5) −2414.2 kJ   13) −258.7 kJ
6) −1390.8 kJ   14) −58.7 kJ
7) −1089.5 kJ   15) −122.6 kJ
8) −592.2 kJ