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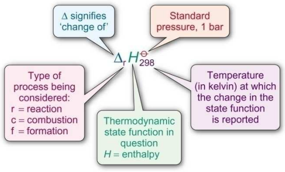
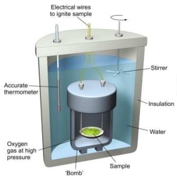


Lecture 6

Calorimetry &Thermochemistry



A commercial bomb calorimeter.

Suggested Reading

Thermochemistry

- Chemistry^3 , Chapter 14, Energy and Thermochemistry, pp.658-700.
- Elements of Physical Chemistry, 5th edition, Atkins & de Paula, Chapter 3, Thermodynamics: applications of the first law. pp. 63-82. Chapter 4. Thermodynamics: The Second Law, pp.83-104.
- Physical Chemistry, 8th Edition, Atkins & de Paula, The First Law, Chapter 2, pp.49-57 (Thermochemistry). Chapter 3, The Second Law, pp.76-116 (selected sections as indicated).
- Chemistry and Chemical Reactivity, Kotz, Treichel, Townsend, 7th edition, Chapter 5, pp.208-253, especially sections 5.7 and 5.8..

Refer to JF Chemistry 1101 laboratory manual thermochemistry experiment # 5
For further details.

Kotz, section 5.2. pp.215-218.

HEAT CAPACITY

The heat required to raise an object's Temperature by 1 °C.

Which has the larger heat capacity?

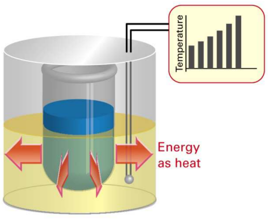
Heat Capacity

Increasing temperature increases the internal energy of a system. The exact increase depends upon the heating conditions.
Heat cannot be detected or measured directly. There is no 'heat meter'.
One way to determine the magnitude of a heat transfer is to measure the work needed to bring about the same change in the thermodynamic state of a system as was produced by heat transfer.
Another approach is to deduce the magnitude of a heat transfer from its effects: namely, a temperature change. When a substance is heated the temperature typically rises. For a specified energy q transferred by heating, the magnitude of the resulting temperature change ΔT depends on the heat capacity C of the substance.
We can therefore simply measure the heat absorbed or released by a system :
We determine the temperature change and use the appropriate value of the heat capacity of the system.
Units of C are J K^{-1}.
Heat capacity is an extensive property.

$$\boxed{C = \frac{q}{\Delta T}}$$

$$\boxed{q = C\Delta T}$$

Can also define specific heat capacity c according to c = C/m where m = mass of substance with units
J $K^{-1}g^{-1}$ or the molar heat capacity C_m as C_m = C/n with units: J $K^{-1}mol^{-1}$.
The heat capacity depends on whether a sample is maintained at constant volume ($C = C_V$) or constant pressure ($C = C_P$). The respective molar quantities are $C_{V,m}$ and $C_{P,m}$.



Loss of energy into the surroundings can be detected by noting whether the temperature changes as the process proceeds.
This is the principle of a calorimeter.

The bomb calorimeter

From the first law of thermodynamics we recall

$$\boxed{\Delta U = q + w = q - P\Delta V}$$

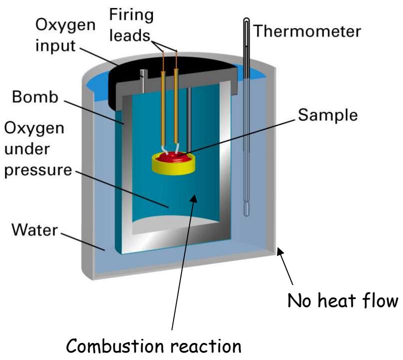
If the reaction is performed in a closed container called a <u>bomb calorimeter</u> then the volume remains constant and $\Delta V = 0$.
Hence the first law reduces to

$$\boxed{\Delta U = q_V}$$

Hence to measure a change in internal energy we should use a fixed volume calorimeter and monitor the energy released ($q < 0$) or supplied ($q > 0$) as heat by measuring the corresponding change in temperature.

Chemistry^3, Ch.14. pp.693-698

Kotz, section 5.6. pp.229-233.



$$\boxed{\begin{aligned} C_V &= \frac{q_V}{\Delta T} = \frac{\Delta U}{\Delta T} \\ C_V &= \lim_{\Delta T \to 0} \frac{\Delta U}{\Delta T} = \frac{dU}{dT} = \left(\frac{\partial U}{\partial T}\right)_V \end{aligned}}$$

Calorimetry : some details.

<u>Calorimetry</u> defines the study of heat transfer during physical and chemical processes.
A calorimeter is a device for measuring energy transferred as heat.
In an adiabatic bomb calorimeter the process which we wish to study (a chemical reaction) is initiated inside a constant volume container (the bomb). The latter is immersed inside a stirred water bath. The whole arrangement (container + water bath) defines the calorimeter. The calorimeter is also immersed in an outer water bath. The water in the calorimeter and in the outer water bath is monitored and adjusted to the same temperature. This arrangement ensures there is no net loss of heat from the calorimeter to the surroundings (the bath). Hence the calorimeter is adiabatic.
The change in temperature ΔT of the calorimeter is proportional to the heat that the reaction releases or absorbs. Hence by measuring ΔT we can determine q_V and hence find ΔU.

We calibrate the calorimeter using a process of known energy output and determining the calorimeter constant C in the relation $q = C\Delta T$.
The calorimeter constant may be measured electrically by passing a constant current I from a source of known potential difference V through a heater for a given period of time t and noting that $q = VIt$.
Alternatively C may be determined by burning a known mass of substance (benzoic acid is often used) that has a known heat output.
With C determined is is simple to interpret an observed temperature rise as a release of heat.

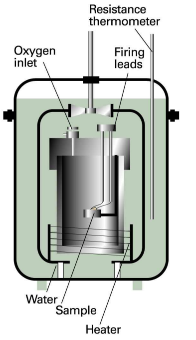
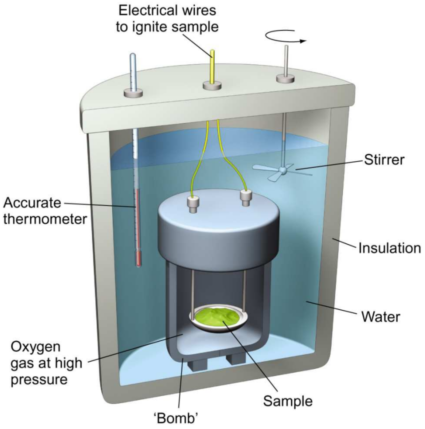
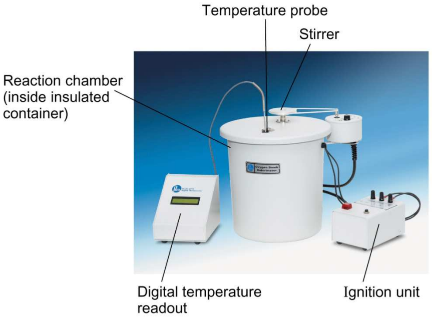
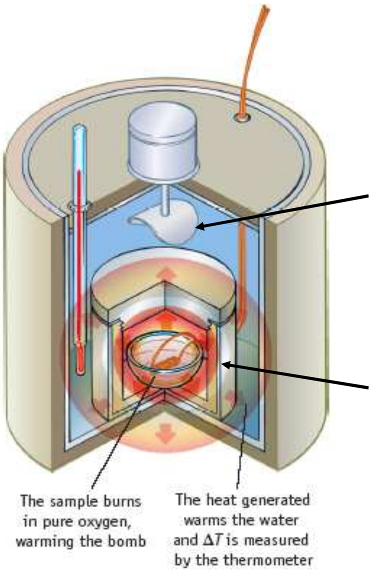


Fig. 2.9 A constant-volume bomb calorimeter. The 'bomb' is the central vessel, which is strong enough to withstand high pressures. The calorimeter (for which the heat capacity must be known) is the entire assembly shown here. To ensure adiabaticity, the calorimeter is immersed in a water bath with a temperature continuously readjusted to that of the calorimeter at each stage of the combustion.





A commercial bomb calorimeter..



Calorimetry

Some heat from reaction warms water

q_{water} = (sp. ht.)(water mass)(ΔT)

Some heat from reaction warms "bomb"

q_{bomb} = (heat capacity, J/K)(ΔT)

Total heat evolved = $q_{total} = q_{water} + q_{bomb}$

Measuring Heats of Reaction
CALORIMETRY

Calculate energy of combustion (ΔU) of octane.

$C_8H_{18} + 25/2\ O_2 \rightarrow CO_2 + 9\ H_2O$

- Burn 1.00 g of octane
- Temp rises from 25.00 to 33.20 °C
- Calorimeter contains 1200. g water
- Heat capacity of bomb = 837 J/K

JF CH1101 Annual 2010 part d.

Measuring Heats of Reaction
CALORIMETRY

Step 1 Calc. energy transferred from reaction to water.

q = (4.184 J/g·K)(1200 g)(8.20 K) = 41,170 J

Step 2 Calc. energy transferred from reaction to bomb.

q = (bomb heat capacity)(ΔT)

= (837 J/K)(8.20 K) = 6860 J

Step 3 Total energy evolved

41,200 J + 6860 J = 48,060 J

Energy of combustion (ΔU) of 1.00 g of octane

= - 48.1 kJ

Enthalpy

Kotz, pp.225-229.

The change in internal energy is not equal to the energy transferred as heat when the system is free to change its volume. Under such circumstances some of the energy supplied as heat to the system is returned to the surroundings as expansion work.

We shall show that under constant pressure conditions, the energy supplied as heat is equal to the change in another thermodynamic property of the system, called the **enthalpy**.

From the first law of thermodynamics for a finite change at constant pressure

$$\boxed{\Delta U = q + w = q_P - P\Delta V}$$

Now $\Delta U = U_F - U_I \quad \Delta V = V_F - V_I$

Hence

$$U_F - U_I = q_P - P(V_F - V_I) = q_P - PV_F + PV_I$$
$$q_P = (U_F + PV_F) - (U_I + PV_I) = H_F - H_I = \Delta H$$

Here we have introduced the enthalpy function H as

$$\boxed{H = U + PV}$$

Hence the heat absorbed at constant pressure equals the increase in enthalpy of the system.

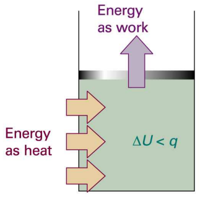


Fig. 2.12 When a system is subjected to constant pressure and is free to change its volume, some of the energy supplied as heat may escape back into the surroundings as work. In such a case, the change in internal energy is smaller than the energy supplied as heat.

$$\boxed{q_P = \Delta H}$$

For an exothermic reaction ΔU < 0, ΔH < 0, whereas for an endothermic reaction, ΔU > 0 and ΔH > 0.

Relationship between ΔU and ΔH.

The enthalpy is given by

$$H = U + PV$$

For a finite change at constant pressure

$$\Delta H = \Delta(U + PV) = \Delta U + \Delta(PV)$$
$$= \Delta U + P\Delta V + V\Delta P$$
$$= \Delta U + P\Delta V$$

ΔP=0
Constant P

Since $\Delta H = q_P \quad \Delta U = q_V$ we note that

$$\boxed{q_P = q_V + P\Delta V}$$

Hence the heat absorbed at constant pressure Exceeds that absorbed at constant volume by the Amount PΔV.
For condensed phases (liquids, solids) $\Delta V = V_{products} - V_{reactants}$ Will be very small and so ΔV ~0. Hence

$$\boxed{\Delta H \cong \Delta U}$$

Condensed phases

Temperature variation of enthalpy.

The term ΔV is significant for gases.

Assume ideal gas behaviour. At constant T and P we have

$$PV = nRT$$

For reactants and products

$$PV_{Rx} = n_{Rx}RT$$
$$PV_{\mathrm{Pr}} = n_{\mathrm{Pr}}RT$$

Hence

$$P(V_{\mathrm{Pr}} - V_{Rx}) = (n_{\mathrm{Pr}} - n_{Rx})RT = \Delta nRT$$

where

$$\Delta n = n_{\mathrm{Pr}} - n_{Rx}$$

Hence for gas phase species

$$\boxed{\Delta H = \Delta U + \Delta nRT}$$

$$\boxed{\begin{aligned} C_P &= \frac{q_P}{\Delta T} = \frac{\Delta H}{\Delta T} \\ C_V &= \lim_{\Delta T \to 0} \frac{\Delta H}{\Delta T} = \frac{dH}{dT} = \left(\frac{\partial H}{\partial T}\right)_P \end{aligned}}$$

Thermochemistry

Thermochemistry is the branch of thermodynamics which studies heats of reaction: heat produced by or required for a chemical reaction.
In thermochemistry, chemical reactions are divided into two categories:

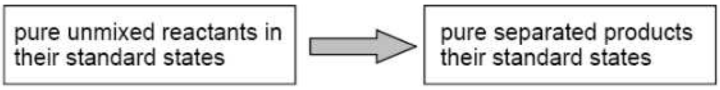
exothermic reaction
$q_{rxn} < 0$; heat is produced by the reacting system (i.e., the temperature of the system is higher right after the reaction than initially; heat must be transferred from the system to the surroundings in order to return the system to its initial temperature)

endothermic reaction
$q_{rxn} > 0$; heat is absorbed by the reacting system (i.e., the temperature of the system is lower right after the reaction than initially; heat must be transferred from the surroundings to the system in order to return the system to its initial temperature)

These reactions can also be described in terms of **enthalpy**, ΔH

Enthalpies of Chemical Change

standard reaction enthalpy, $\Delta_r H^o$:
Change in enthalpy when reactants in standard states change to products in standard states



pure unmixed reactants in their standard states

pure separated products their standard states

Example:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \quad \Delta_r H^o = -890 \text{ kJ mol}^{-1}$$

The change in enthalpy for the above **thermochemical equation** is for 1 mole of pure $CH_4(g)$ reacting with 2 moles of pure $O_2(g)$ at 1 bar to produce 1 mole of pure $CO_2(g)$ and 2 moles of pure $H_2O(l)$ at 1 bar

Changes in enthalpies of mixing and separation are insignificant compared to the standard reaction enthalpy, and may be neglected in this case

Hess's Law

Kotz, section 5.7, pp.233-239

Chemical reactions involve emission or adsorption of heat energy.
We now discuss how these energy changes are calculated.
Many chemical reactions are performed under conditions of constant pressure, so it is best to describe heat changes in terms of changes in enthalpy since $q_P = \Delta H$.

Enthalpy is a state function. As such ΔH going from some initial state to some final state is pathway independent so we can use any suitable pathway when calculating the enthalpy change associated with a chemical reaction.

Hence in going from a particular set of reactants to a particular set of products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.
This principle is known as **Hess's law**.

To use Hess's Law to compute enthalpy changes for reactions we note:

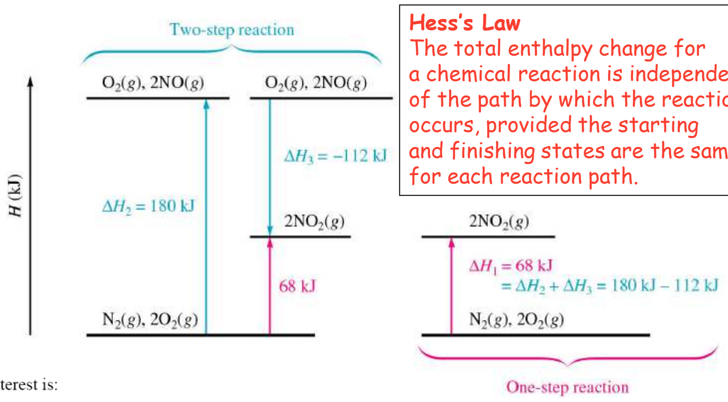
1. If a reaction is reversed, the sign of ΔH is also reversed.
2. The magnitude of ΔH is directly proportional to the quantities of reactants and products in a reaction. If the coefficients in a balanced reaction are multiplied by an integer, the value of ΔH is multiplied by the same integer.

Formation of nitrogen dioxide.

Hess' Law: An Example

$N_2 + 2O_2 \rightleftarrows 2NO_2$ The brown gas in photochemical smog.

Hess's Law
The total enthalpy change for a chemical reaction is independent of the path by which the reaction occurs, provided the starting and finishing states are the same for each reaction path.



- Our reaction of interest is:

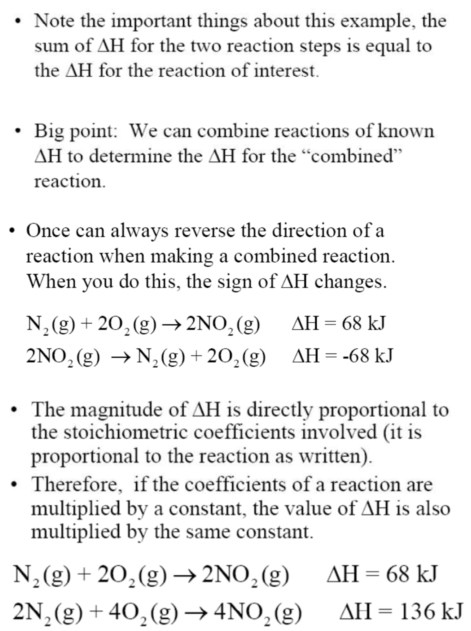
$N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g) \quad \Delta H = 68$ kJ

- This reaction can also be carried out in two steps:

$N_2(g) + O_2(g) \longrightarrow 2NO(g) \quad \Delta H = 180$ kJ
$2NO(g) + O_2(g) \longrightarrow 2NO_2(g) \quad \Delta H = -112$ kJ

- If we take the previous two reactions and add them, we get the original reaction of interest:

$$\begin{array}{ll} N_2(g) + O_2(g) \longrightarrow \cancel{2NO}(g) & \Delta H = 180 \text{ kJ} \\ \cancel{2NO}(g) + O_2(g) \longrightarrow 2NO_2(g) & \Delta H = -112 \text{ kJ} \\ \hline N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g) & \Delta H = 68 \text{ kJ} \end{array}$$



- Note the important things about this example, the sum of ΔH for the two reaction steps is equal to the ΔH for the reaction of interest.

- Big point: We can combine reactions of known ΔH to determine the ΔH for the "combined" reaction.

- Once can always reverse the direction of a reaction when making a combined reaction. When you do this, the sign of ΔH changes.

$N_2(g) + 2O_2(g) \rightarrow 2NO_2(g) \quad \Delta H = 68\ kJ$

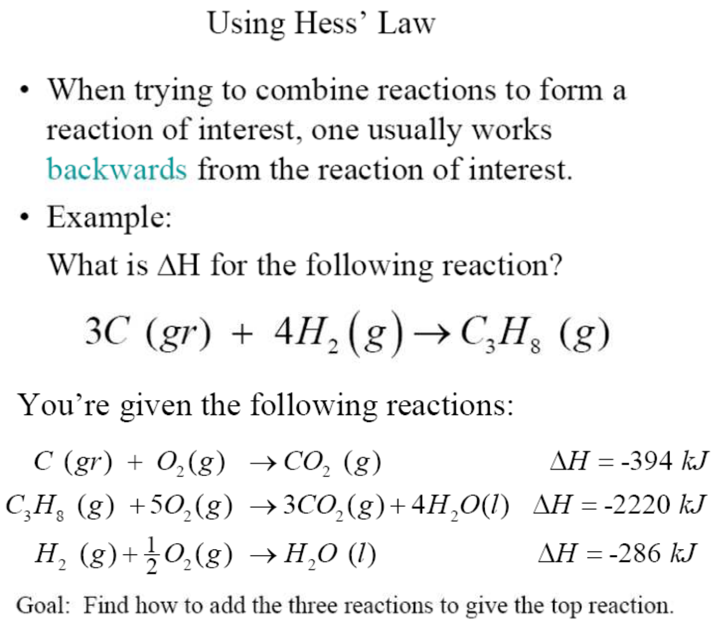
$2NO_2(g) \rightarrow N_2(g) + 2O_2(g) \quad \Delta H = -68\ kJ$

- The magnitude of ΔH is directly proportional to the stoichiometric coefficients involved (it is proportional to the reaction as written).
- Therefore, if the coefficients of a reaction are multiplied by a constant, the value of ΔH is also multiplied by the same constant.

$N_2(g) + 2O_2(g) \rightarrow 2NO_2(g) \quad \Delta H = 68\ kJ$

$2N_2(g) + 4O_2(g) \rightarrow 4NO_2(g) \quad \Delta H = 136\ kJ$

Enthalpy of formation of propane



Using Hess' Law

- When trying to combine reactions to form a reaction of interest, one usually works backwards from the reaction of interest.
- Example:

  What is ΔH for the following reaction?

$$3C\ (gr)\ +\ 4H_2(g) \rightarrow C_3H_8\ (g)$$

You're given the following reactions:

$$C\ (gr)\ +\ O_2(g)\ \rightarrow CO_2\ (g) \qquad \Delta H = -394\ kJ$$

$$C_3H_8\ (g)\ + 5O_2(g)\ \rightarrow 3CO_2(g) + 4H_2O(l) \quad \Delta H = -2220\ kJ$$

$$H_2\ (g) + \tfrac{1}{2}O_2(g)\ \rightarrow H_2O\ (l) \qquad \Delta H = -286\ kJ$$

Goal: Find how to add the three reactions to give the top reaction.

Approach: Find a thread through the equation for each starting and ending material. Eg: follow C(gr) to C_3H_8. Follow H_2 to C_3H_8. Use the target reaction as your way of finding the path that connects reactants and products.

- Step 1. Only reaction 1 has C (gr). Therefore, we will multiply by 3 to get the correct amount of C (gr) with respect to our final equation.

Initial:

$$C\ (gr) + O_2\ (g) \longrightarrow CO_2\ (g) \quad \Delta H = -394\ kJ$$

Final:

$$3C\ (gr) + 3O_2\ (g) \longrightarrow 3CO_2\ (g) \quad \Delta H = -1182\ kJ$$

- Step 2. To get C_3H_8 on the product side of the reaction, we need to reverse reaction 2.

Initial:

$$C_3H_8\ (g) + 5O_2\ (g) \longrightarrow 3CO_2\ (g) + 4H_2O\ (l) \quad \Delta H = -2220\ kJ$$

Final:

$$3CO_2\ (g) + 4H_2O\ (l) \longrightarrow C_3H_8\ (g) + 5O_2\ (g) \quad \Delta H = +2220\ kJ$$

- Step 3: Add two "new" reactions together to see what is left:

$$3C\ (gr) + \cancel{3O_2}\ (g) \longrightarrow \cancel{3CO_2}\ (g) \quad \Delta H = -1182\ kJ$$

$$\cancel{3CO_2}\ (g) + 4H_2O\ (l) \longrightarrow C_3H_8\ (g) + \underset{2}{\cancel{5}}O_2\ (g) \quad \Delta H = +2220\ kJ$$

$$3C\ (gr) + 4H_2O\ (l) \longrightarrow C_3H_8\ (g) + 2O_2 \quad \Delta H = +1038\ kJ$$

- Step 4: Compare previous reaction to final reaction, and determine how to reach final reaction:

$$3C\ (gr) + 4H_2O\ (l) \longrightarrow C_3H_8\ (g) + 2O_2 \qquad \Delta H = +1038\ kJ$$
$$H_2\ (g) + 1/2O_2\ (g) \longrightarrow H_2O\ (l) \qquad \Delta H = -286\ kJ$$

$$3C\ (gr) + 4H_2\ (g) \longrightarrow C_3H_8\ (g)$$

Need to get rid of O_2:
multiply second reaction by 4

$$3C\ (gr) + 4H_2O\ (l) \longrightarrow C_3H_8\ (g) + 2O_2 \qquad \Delta H = +1038\ kJ$$
$$4H_2\ (g) + 2O_2\ (g) \longrightarrow 4H_2O\ (l) \qquad \Delta H = -1144\ kJ$$

$$3C\ (gr) + 4H_2\ (g) \longrightarrow C_3H_8\ (g)$$

$$3C\ (gr) + \cancel{4H_2O}\ (l) \longrightarrow C_3H_8\ (g) + \cancel{2O_2} \qquad \Delta H = +1038\ kJ$$
$$4H_2\ (g) + \cancel{2O_2}\ (g) \longrightarrow \cancel{4H_2O}\ (l) \qquad \Delta H = -1144\ kJ$$

$$3C\ (gr) + 4H_2\ (g) \longrightarrow C_3H_8\ (g) \qquad \Delta H = -106\ kJ$$

Standard Enthalpy Changes

Numerical values describing ΔU or ΔH of a system when some chemical or physical change occurs depend upon the nature of the reaction, as well as the physical states of reactants and products

It is useful to define a **standard enthalpy change**, ΔH^o, which is the change in enthalpy for a process (chemical or physical) where initial and final substances are in **standard states**

standard states: pure form of a substance at specified temperature at pressure of 1 bar, e.g. standard state of liquid water at 298 K is pure liquid water at 298 K and 1 bar

Examples: The standard enthalpy of ***vapourization***, $\Delta_{vap}H^o$, is change in enthalpy per mole when pure liquid vapourizes to pure gas at pressure of 1 bar. The standard enthalpy of ***fusion***, $\Delta_{fus}H^o$, is enthalpy change accompanying change from liquid to solid

$H_2O(l)$ ¬ $H_2O(g)$ $\qquad \Delta_{vap}H^o(373\ K) = +40.66\ kJ\ mol^{-1}$

$H_2O(s)$ ¬ $H_2O(l)$ $\qquad \Delta_{fus}H^o(273\ K) = +6.01\ kJ\ mol^{-1}$

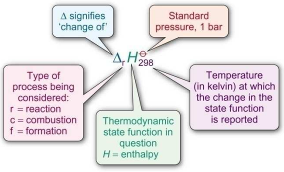
ΔH^o can be reported at any temperature, convention is at 298.15 K

Standard enthalpy of formation/reaction

Chemistry^3 section 14.3
Kotz section 5.5-5.8.

The standard molar enthalpy of formation is the enthalpy change for the formation of 1 mol of a compound directly from its component elements in their standard states.
It is not possible to define an absolute measure of enthalpy so a reference State is needed. By convention the enthalpy of formation of an element in its standard state is zero.
The standard state of an element or a compound is defined as the most stable form of the substance in the physical state that exists at a pressure of 1 bar and at a specified temperature (typically 298 K).

The standard enthalpy of formation $\Delta_f H^0$ of reactants and products may be used to compute the standard enthalpy change for a chemical reaction $\Delta_r H^0$.



Sum of all enthalpy changes of formation of products.

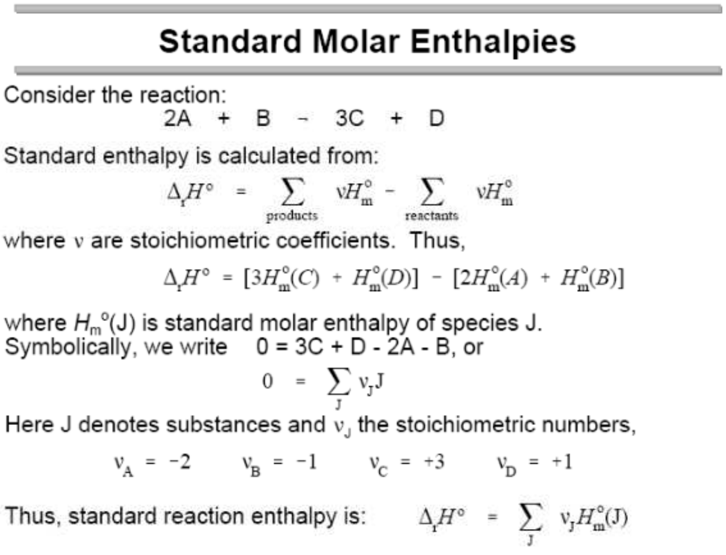
$$\alpha A + \beta B \rightarrow \gamma P + \delta Q$$

$$\Delta_r H^0_{298} = \left\{\gamma \Delta_f H^0_{298}(P) + \delta \Delta_f H^0_{298}(Q)\right\} - \left\{\alpha \Delta_f H^0_{298}(A) + \beta \Delta_f H^0_{298}(B)\right\}$$

$$\boxed{\Delta_r H^0_{298} = \sum \nu_j \Delta_f H^0_{298}(pr) - \sum \nu_j \Delta_f H^0_{298}(rx)}$$

Sum of all enthalpy changes of formation of reactants.

Stoichiometric coefficient



Standard Molar Enthalpies

Consider the reaction:

2A + B – 3C + D

Standard enthalpy is calculated from:

$$\Delta_r H^\circ = \sum_{\text{products}} \nu H^\circ_m - \sum_{\text{reactants}} \nu H^\circ_m$$

where ν are stoichiometric coefficients. Thus,

$$\Delta_r H^\circ = [3H^\circ_m(C) + H^\circ_m(D)] - [2H^\circ_m(A) + H^\circ_m(B)]$$

where $H_m{}^\circ(J)$ is standard molar enthalpy of species J.
Symbolically, we write $0 = 3C + D - 2A - B$, or

$$0 = \sum_J \nu_J J$$

Here J denotes substances and ν_J the stoichiometric numbers,

$$\nu_A = -2 \qquad \nu_B = -1 \qquad \nu_C = +3 \qquad \nu_D = +1$$

Thus, standard reaction enthalpy is: $\Delta_r H^\circ = \sum_J \nu_J H^\circ_m(J)$

Kotz, section 5.3, pp.219-221.

Enthalpy of Physical Change

standard enthalpy of transition, $\Delta_{trs}H^o$:
Standard enthalpy change accompanying a phase change

(**A**) Enthalpy is a *state function*, independent of path between initial and final states: same value of ΔH^o occurs regardless of how change occurs!

melting $H_2O(s) \rightarrow H_2O(l)$ $\Delta_{fus}H^o$
boiling $H_2O(l) \rightarrow H_2O(g)$ $\Delta_{vap}H^o$
sublimation $H_2O(s) \rightarrow H_2O(g)$ $\Delta_{sub}H^o = \Delta_{fus}H^o + \Delta_{vap}H^o$

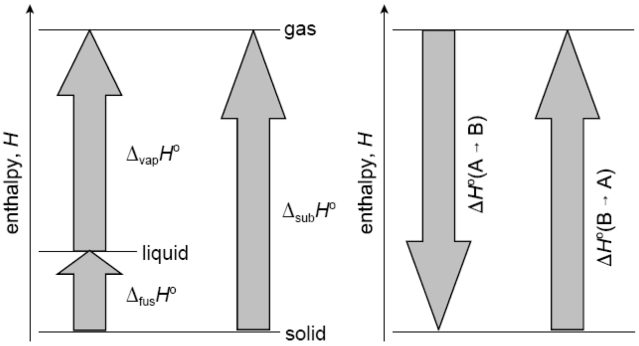
(**B**) Enthalpy is a *state function*, so ΔH^o differs only in sign for forward and reverse processes

$$\Delta H^o(A \rightarrow B) \quad = \quad -\Delta H^o(B \rightarrow A)$$

Example: At 298 K,

condensing $H_2O(g) \rightarrow H_2O(l)$ $\Delta_{vap}H^o = -44 \text{ kJ mol}^{-1}$
boiling $H_2O(l) \rightarrow H_2O(g)$ $\Delta_{vap}H^o = +44 \text{ kJ mol}^{-1}$

Graphical Depiction of Enthalpies of Transition



(**A**) Same ΔH^o, regardless of **pathway**

(**B**) Forward & reverse processes, ΔH^o differs only in sign

Enthalpies of Fusion and Vapourization

See Table 2.3 Atkins 6th Ed. at back of book for a listing of enthalpies of fusion and vapourization, with freezing and boiling temperatures

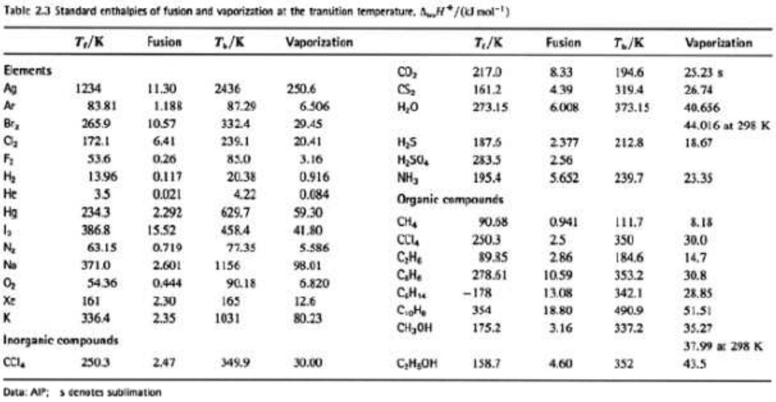


Table 2.3 Standard enthalpies of fusion and vaporization at the transition temperature, $\Delta_{trs}H^{\ominus}/(\mathrm{kJ\,mol^{-1}})$

	T_f/K	Fusion	T_b/K	Vaporization
Elements				
Ag	1234	11.30	2436	250.6
Ar	83.81	1.188	87.29	6.506
Br_2	265.9	10.57	332.4	29.45
Cl_2	172.1	6.41	239.1	20.41
F_2	53.6	0.26	85.0	3.16
H_2	13.96	0.117	20.38	0.916
He	3.5	0.021	4.22	0.084
Hg	234.3	2.292	629.7	59.30
I_2	386.8	15.52	458.4	41.80
N_2	63.15	0.719	77.35	5.586
Na	371.0	2.601	1156	98.01
O_2	54.36	0.444	90.18	6.820
Xe	161	2.30	165	12.6
K	336.4	2.35	1031	80.23
Inorganic compounds				
CCl_4	250.3	2.47	349.9	30.00
CO_2	217.0	8.33	194.6	25.23 s
CS_2	161.2	4.39	319.4	26.74
H_2O	273.15	6.008	373.15	40.656 44.016 at 298 K
H_2S	187.6	2.377	212.8	18.67
H_2SO_4	283.5	2.56		
NH_3	195.4	5.652	239.7	23.35
Organic compounds				
CH_4	90.68	0.941	111.7	8.18
CCl_4	250.3	2.5	350	30.0
C_2H_6	89.85	2.86	184.6	14.7
C_6H_6	278.61	10.59	353.2	30.8
C_6H_{14}	−178	13.08	342.1	28.85
$C_{10}H_8$	354	18.80	490.9	51.51
CH_3OH	175.2	3.16	337.2	35.27 37.99 at 298 K
C_2H_5OH	158.7	4.60	352	43.5

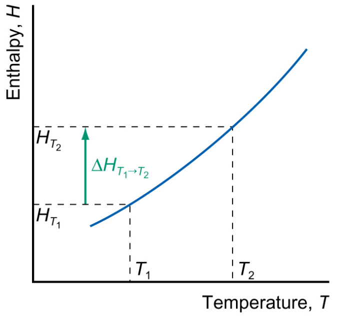
Data: AIP; s denotes sublimation

Enthalpies of Transition †

There are many different types of transitions, each of which has an associated change in enthalpy

Transition	Process	Symbol
Transition	Phase α → Phase β	$\Delta_{trs}H$
Fusion	s → l	$\Delta_{fus}H$
Vapourization	l → g	$\Delta_{vap}H$
Sublimation	s → g	$\Delta_{sub}H$
Mixing fluids	Pure → mixture	$\Delta_{mix}H$
Solution	Solute → solution	$\Delta_{sol}H$
Hydration	$X^{\pm}$(g) → $X^{\pm}$(aq)	$\Delta_{hyd}H$
Atomization	Species(s,l,g) → atoms(g)	$\Delta_{at}H$, $\Delta_{diss}H$
Ionization	X(g) → X^+(g) + e-(g)	$\Delta_{ion}H$
Electron gain	X(g) + e-(g) → X^-(g)	$\Delta_{eg}H$
Reaction	Reactants → products	Δ_rH
Combustion	Cmpd(s,l,g) + O_2(g) → CO_2(g) + H_2O(l,g)	Δ_cH
Formation	Elements → compound	Δ_fH
Activation	Reactants → activated complex	$\Delta^{\ddagger}H$

Variation of enthalpy of a substance with temperature



The enthalpy of a substance increases with temperature. Now enthalpy change is the heat transferred at constant pressure. Let q_P is the energy used to heat a substance in an open container from an initial temperature T_1 to a final temperature T_2. Hence the enthalpy change is

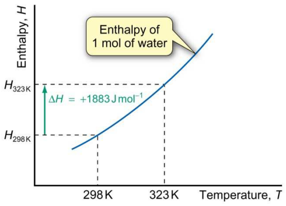
$$\boxed{\Delta H(T_1 \rightarrow T_2) = q_P}$$

Now q_P is given by

$$q_P = nC_{P,m}\Delta T = nC_{P,m}(T_2 - T_1)$$

Hence

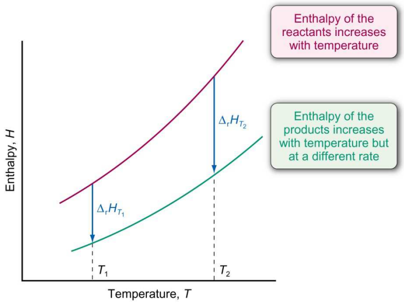
$$\boxed{\begin{aligned}\Delta H(T_1 \rightarrow T_2) &= H(T_2) - H(T_1) \\ &= C_{P,m}\Delta T = C_{P,m}(T_2 - T_1)\end{aligned}}$$



Note that H(T) variation is a curve rather than a straight Line since $C_{P,m}$ also varies with temperature.

Variation of enthalpy of a reaction with temperature: Kirchoff equation.

If the enthalpy chance for a reaction $\Delta_r H(T_1)$ is known at the temp. T_1, then the value $\Delta_r H(T_2)$ at another temp. T_2 can be determined using the Kirchoff equation.



$$\boxed{\Delta_r H^0(T_2) = \Delta_r H^0(T_1) + \Delta C_{P,m}\Delta T}$$

Note that $\Delta C_{P,m}$ denotes the difference between the molar heat capacity of the products and the molar heat capacity of the reactants.

$$\boxed{\Delta C_{P,m} = \sum \nu_j C_{P,m}(pr) - \sum \nu_j C_{P,m}(rx)}$$

Derivation provided in Chemistry^3 Box 14.5 p.683.
See worked example p.684.