

Thermochemistry

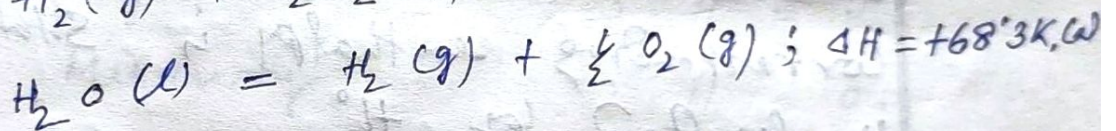
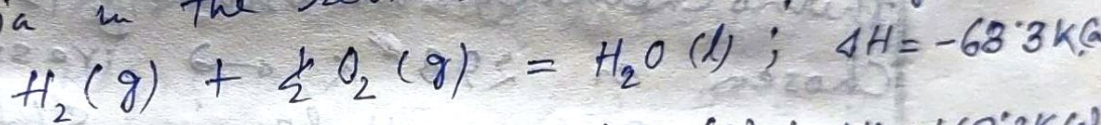
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The laws of Thermochemistry :-

The thermal changes in chemical processes are governed by two general principles, both of which are, of course, Corollaries of the 1st law,

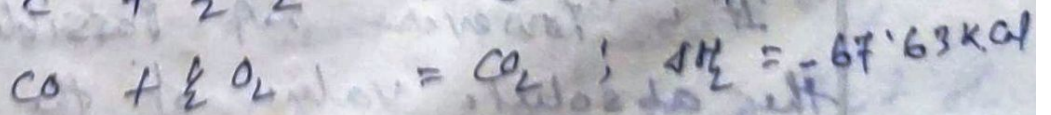
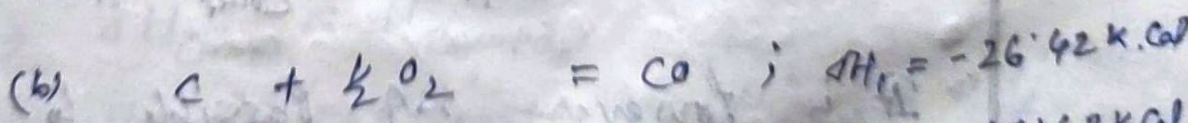
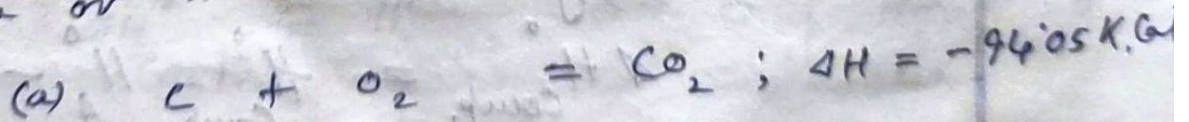
(1) Law of Lavoisier and Laplace :-

This law states that, "the heat change accompanying a chemical process in one direction is equal in magnitude but opposite in sign, to that accompanying the same reaction in the reverse direction." Eg.



✓ (2) Hess's law :-

The law states that, "for a given chemical process, the net heat change (q_p or q_v) will be the same whether the process occurs in one or in several stages." Eg.



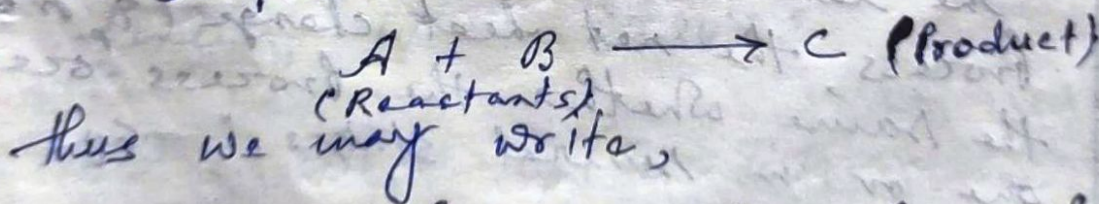
$$\Delta H = \Delta H_1 + \Delta H_2$$

- * Enthalpy of reaction :- See in page 27-30
- * Relation betⁿ H and U :- -do-
- * Standard enthalpy changes :-
- * Relation of reaction enthalpy with change in internal energy :- See in page 29-30

Standard enthalpy :-

The enthalpy of a substance depends upon Press^r and temp^r. The standard temp^r for thermochemical measurements has been chosen as $298^{\circ}K$ and Press^r 1 atm, and corresponding enthalpy is standard enthalpy, is denoted by H° .

Say, the elements A & B unite to form a compound C i.e.



$$\Delta H_{\text{comp}}^{\circ} = H_{\text{Comp}}^{\circ} - H_A^{\circ} - H_B^{\circ}$$

It is however not possible to determine the absolute value of the standard enthalpy (H°) of a substance. In order to measure

the change in enthalpy, it is therefore necessary to assume some arbitrary value at a given state. It has been decided to assign the value "zero" for the enthalpy for every element at 1 atm and 298°K,

When elements occur in different modifications, the most stable form is given the value 'zero'. Eg. at 298°K and 1 atm,

Carbon (graphite) ; $H^\circ = 0$

Sulphur (rhombic) ; $H^\circ = 0$

Magnesium ; $H^\circ = 0$

Mercury ; $H^\circ = 0$

Oxygen ; $H^\circ = 0$

Nitrogen ; $H^\circ = 0$

with this convention, we have,

$$\Delta H^\circ_{\text{Compd.}} = H^\circ_{\text{Compd.}} - 0 - 0 \quad | \quad \because H^\circ_A = H^\circ_B = 0$$

$$\Rightarrow \Delta H^\circ_{\text{Compd.}} = H^\circ_{\text{Compd.}}$$

$$\Rightarrow H^\circ_{\text{Compd.}} = \Delta H^\circ_{\text{Compd.}} \Rightarrow H^\circ_{\text{Compd.}} = \Delta H^\circ_f$$

\therefore The std. enthalpy of compd. = stand. heat of formation

* Various types of Enthalpies of Reaction :-

The heat of reaction at constant pressure (q_p) is really the enthalpy change of a chemical process. (ie. $q_p = \Delta H$). The enthalpy changes in different chemical processes have been given different names according to the type of reaction. Such as,

- (I) Heat of formation, ΔH_f
(enthalpy)
- (II) Heat of Combustion, ΔH_c
(enthalpy)
- (III) Heat of Neutralisation, ΔH_n
(enthalpy)
- (IV) Heat of Solution, ΔH_s
(enthalpy)
- (V) Heat of Transition, ΔH^{\ddagger}
(enthalpy)

Besides these there are several types of enthalpies of reaction such as -

- (vi) Enthalpy of hydration
- (vii) Enthalpy of ionisation
- (viii) Enthalpy of precipitation etc.

(i) Heat/enthalpy of formation :-

The enthalpy change occurring when a gm. molecule of a substance is formed from its constituent elements is called its "heat of formation".

When heat is evolved in the formation of a compound from the elements, the compd. is called an exothermic and if heat is absorbed in the formation of a compd. from the elements, it is called an endothermic substance.

It is denoted by, ΔH_f . eg.

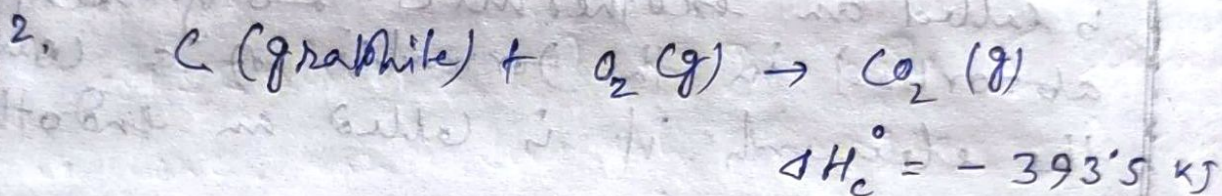
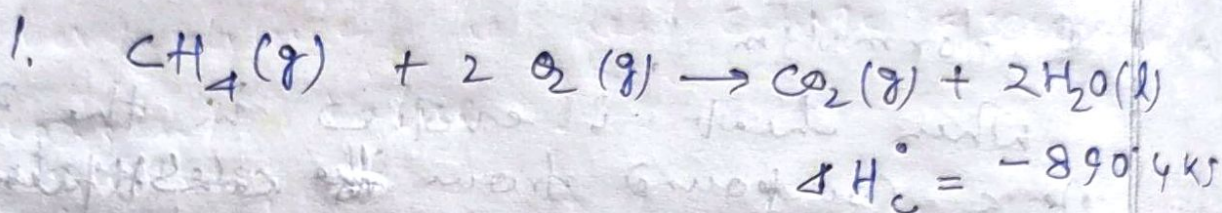
1. $C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g); \Delta H_f^\circ = -393.5 \text{ kJ}$
2. $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l); \Delta H_f^\circ = -285.8 \text{ kJ}$
3. $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l); \Delta H_f^\circ = -890.4 \text{ kJ}$

(ii) Heat/enthalpy of combustion :-

The enthalpy of combustion of a given compd. is defined as the enthalpy change when one mole of this compd. combines with requisite

amount of oxygen to give products in their stable forms.

It is denoted by ΔH_c Eg.

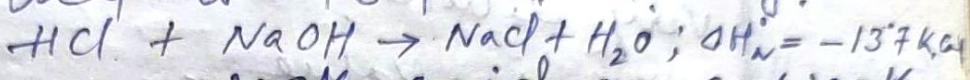


(iii) Heat / enthalpy of - Neutralisation :-

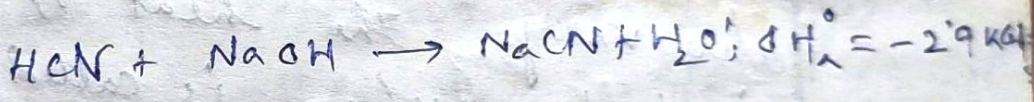
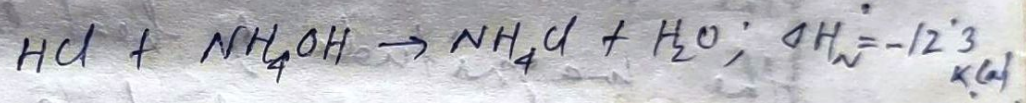
Neutralisation of an acid or a base is always an exothermic process. The amount of heat liberated when one gm-equiv. of an acid is neutralised by a gm-equiv. of base is called the heat of neutralisation, i.e. ΔH_n .

Heat of neutralisation is really the heat of formation of a gm-mole of water from a gm-ion of hydrogen and gm ion

of hydroxyl ion. This is confirmed from the fact that the heat of neutralisation of any strong acid by any strong base in dilute solutions is always the same and is equal to 13.7 K. Cal. eg.



But, when a weak acid or a weak base is neutralised, the heat of neutralisation deviates considerably from the value of 13.7 K. Cal. Eg.



This is due to the fact, that a weak acid or base is very slightly dissociated, and a portion of the energy is utilised in the process of dissociation of the weak counterpart as the reaction proceeds.

(IV) Heat/enthalpy of Solution :-

The net thermal change occurs when one gm-mole of the solute is completely dissolved in a solvent is called the

heat of solution, or more appropriately the integral heat of solution, i.e. ΔH_s .

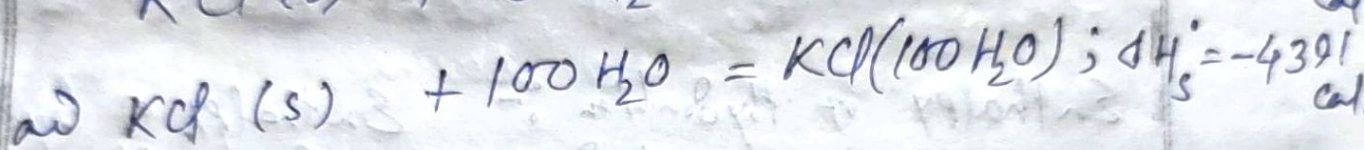
The heat of solⁿ is however changes with concentration. When the solⁿ become very dilute, the heat change assumes a constant value.

It is obvious that, during the process of dissolution of a 1m mole of solute, the conc. continuously changes and hence the magnitude of heat changes would also vary. The heat of solⁿ at any instant $\Delta H/\Delta n$ is called the differential heat of solⁿ. This is indeed a partial molar quantity.

Since the heat of solⁿ varies with conc. the addition of a quantity of solute to a given solⁿ fairly high conc. would involve a thermal change.

The net heat change associated with the dilution of a solⁿ containing 1 mole of solute from a conc. c_1 to

another conc. C_2 is called the integral heat of dilution. The integral heats of dilution are evidently the differences of the heats of solⁿ at the corresponding conc. Eg.



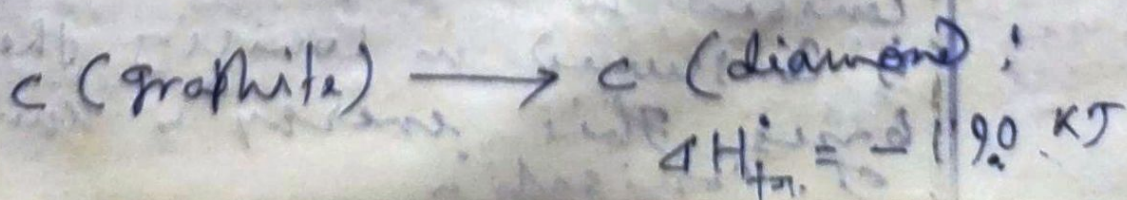
By subtraction,



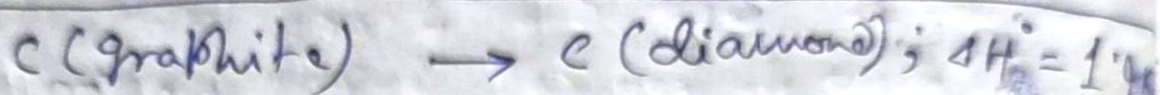
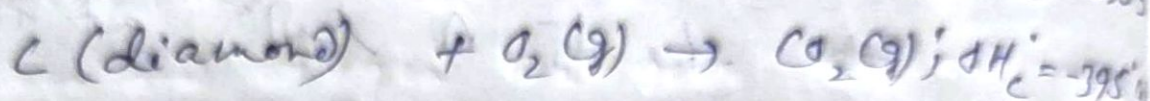
ie. in diluting KCl (50H₂O) solⁿ to half of its conc. (to KCl 100H₂O) solⁿ. another 115 cal of heat would be absorbed.

(V) Heat/enthalpy of Transition :-

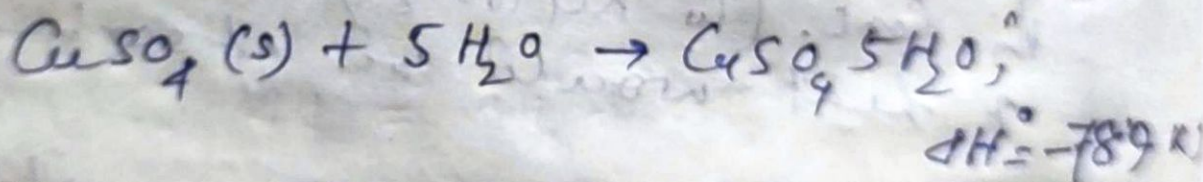
Enthalpy of transition is the heat-(enthalpy) change, when one mole of one allotropic form changes to another form. Eg.



This is obtained as,

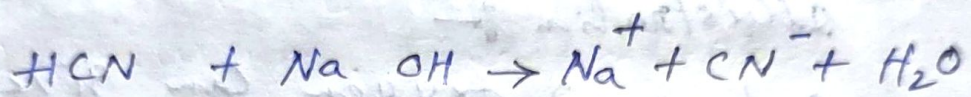


Enthalpy of hydration :- Enthalpy of hydration of a given anhydrous or partially hydrated salt is the enthalpy change when it combines with the requisite amount of water to form a new hydrated stable salt. eg.



Enthalpy of Ionisation :- Whenever a weak acid (or base) reacts with a strong base (or acid), the release of heat is less than 57.3 kJ . It is because of the fact that these acids or bases are not completely ionised in solⁿ, some of the heat is consumed in ionising these acids or bases. This energy is known as enthalpy of ionisation.

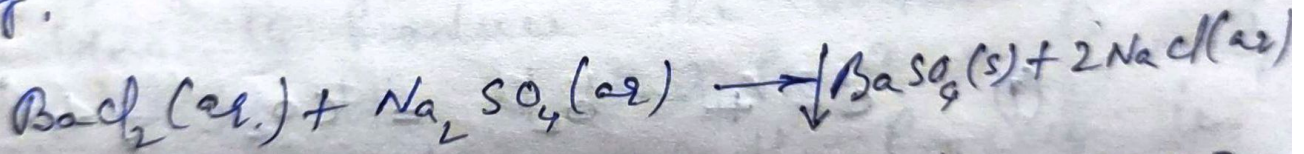
Eg.



$$\Delta H^\circ = -12.13 \text{ kJ}$$

Enthalpy of Precipitation :- Enthalpy of precipitation is the enthalpy change when one mole of a precipitate is formed.

Eg.



$$\Delta H^\circ = -24.3 \text{ kJ}$$