



ADVANCED CHEMISTRY BLOC

(THERMOCHEMISTRY)

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Chemical reactions are generally performed at a constant pressure of 1 atm. The heat flow, q_p between the system and the surroundings is therefore, equal to change in enthalpy, ΔH . However, for reactions at constant volume, we have $q_v = \Delta U$, where ΔU may be converted into ΔH by using the relation,

$$\Delta H = \Delta U + \Delta n_g RT$$

In a chemical reaction taking place at a constant pressure, there is generally a difference in temperature before and after the reaction. To restore the system to its initial temperature, heat must flow either to or from the surroundings. Accordingly, exothermic reactions evolve heat whereas endothermic reactions absorb heat. The study of enthalpy for different types of chemical reactions is known as thermochemistry. As enthalpy ' H ' is an extensive property, the change in enthalpy of the reaction, ΔH , is usually reported for 1 mole of the reactant or product. In thermochemistry, we often deal with ΔH and not with ΔU as chemical reactions are generally carried out at constant pressure.

Standard Enthalpy Changes in Different Processes

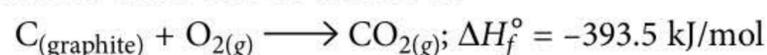
There is no way to measure the absolute value of the enthalpy of a substance. Only values relative to an arbitrary reference can be determined to assign enthalpy values to various substances.

The reference point for all enthalpy expressions is called standard enthalpy of formation, ΔH_f° . The reference form is usually the most stable form of the elements. By convention, the enthalpy of formation of the most stable form of an element in its standard state is zero at every temperature. The elements are said to be in standard state at 1 atm, hence the term standard enthalpy is being used. Although the standard state does not specify a temperature, we always use ΔH_f° values measured at 25°C.

For oxygen, O_2 is more stable than O_3 at 1 atm and 25°C, therefore $\Delta H_f^\circ(O_2) = 0$ but $\Delta H_f^\circ(O_3) \neq 0$.

Similarly, for the element carbon, graphite is more stable than diamond, hence $\Delta H_f^\circ(C, \text{graphite}) = 0$ but $\Delta H_f^\circ(C, \text{diamond}) \neq 0$. The reference form of S, P and Br_2 are rhombic S, black P and liquid Br_2 respectively.

Thus defining ΔH_f° as zero for all elements at standard state, 1 atm establishes a reference point from which ΔH_f° values for different substances can be measured. For example, the enthalpy of formation of a mole of $CO_{2(g)}$ from its elements C and O_2 in their standard states can be written as



$$\text{or } \Delta H_f^\circ(CO_2) = H^\circ(CO_2) - \{H^\circ(C) + H^\circ(O_2)\}$$

As standard enthalpies of C and O_2 are zero,

$$\Delta H_f^\circ(CO_2) = H^\circ(CO_2)$$

For a hypothetical reaction,



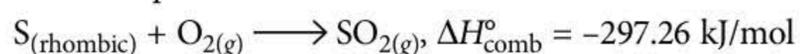
the standard enthalpy of reaction, ΔH_r° can be calculated as

$$\Delta H_r^\circ = \{m\Delta H_f^\circ(M) + n\Delta H_f^\circ(N)\} - \{a\Delta H_f^\circ(A) + b\Delta H_f^\circ(B)\}$$

Enthalpy (Heat) of Combustion

The heat of combustion of a substance is defined as the heat evolved when 1 mole of that substance is burnt completely in oxygen.

For example,



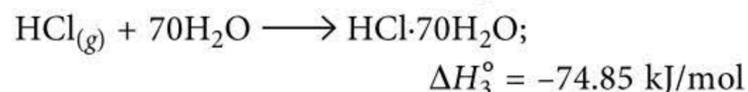
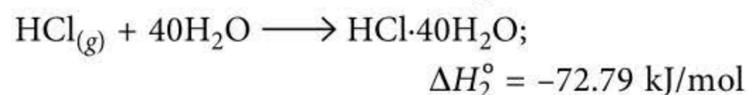
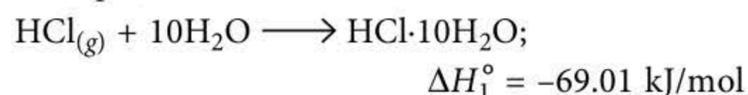
Combustion processes are generally exothermic, and hence $\Delta H_{\text{comb}}^\circ$ is used to determine the fuel values. The heat of combustion is measured at constant volume. So, ΔU is obtained which is then converted to ΔH .

Enthalpy (Heat) of Solution and Dilution

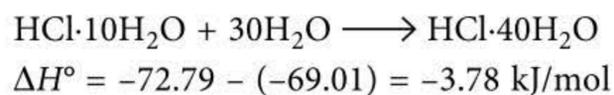
The formation of a solution is either accompanied with absorption or liberation of heat. The heat of solution is the enthalpy change when 1 mole of a solute is dissolved in a specified amount of a solvent

at a constant temperature and pressure. This enthalpy of solution is called the integral heat of solution, which depends on the amount of the solvent per mole of the solute.

For example,

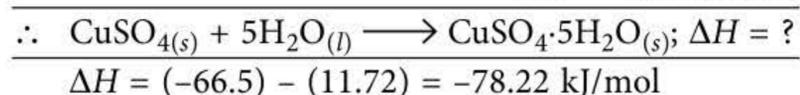
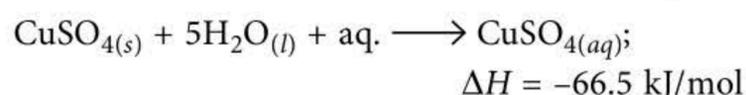
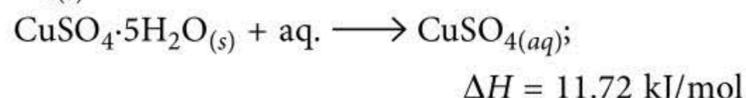


On adding more and more solvent, ΔH° value increases and approaches a limiting value at infinite dilution. ΔH_3° gives the integral heat of solution at infinite dilution and represents the upper limit of the heat released. The integral heat of dilution is defined as the change in enthalpy when a solution of known concentration is diluted by adding more solvent. For example, when 30 moles of H_2O are added to $\text{HCl}\cdot 10\text{H}_2\text{O}$ solution, the enthalpy change is calculated by subtracting the above two equations.



Enthalpy (Heat) of Hydration

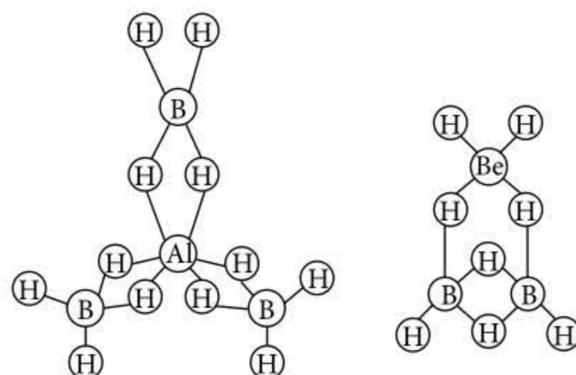
The heat of hydration is defined as the heat change accompanying the formation of 1 mole of a specified hydrate from 1 mole of its anhydrous substance. This is calculated from the enthalpies of solutions of hydrous and anhydrous substances. For example, from the values of enthalpies of solutions of $\text{CuSO}_4\cdot 5\text{H}_2\text{O}_{(s)}$ and $\text{CuSO}_{4(s)}$ we can calculate the enthalpy of hydration of $\text{CuSO}_{4(s)}$.



Enthalpy of neutralisation and enthalpy of formation are very common concepts. So we have consciously dropped them from this discussion.

CHEMISTRY MUSING

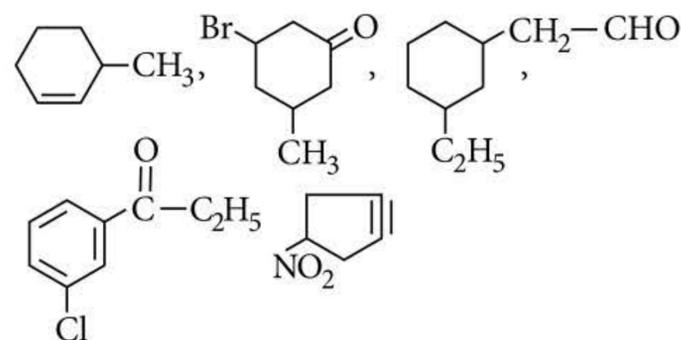
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7. Select the incorrect statement from the following.
- Hybridisation of Al in $\text{Li}[\text{AlH}_4]$ is same as B in $\text{Na}[\text{BH}_4]$.
 - Geometry around Al in $\text{Li}[\text{AlH}_4]$ is same as AlCl_4^- .
 - AlH_4^- , BH_4^- , AlCl_4^- are iso-structural.
 - AlH_4^- , AlCl_4^- , BH_4^- are iso-electronic.
8. Select the correct statement about $\text{Al}(\text{BH}_4)_3$.
- Each tetrahydridoborate ion forms two hydrogen bridges.
 - Two BH_4 form 2 hydrogen bridges and one BH_4 forms one hydrogen bridge.
 - One BH_4 forms 2 hydrogen bridges and two BH_4 form one hydrogen bridge.
 - B forms only $2c - 2e$ bond.

INTEGER VALUE

9. How many organic compounds given below will exhibit both Wolff-Kishner reduction as well as nucleophilic addition reaction?



10. In a certain reaction, B^{n+} is getting converted to $B^{(n+4)+}$ in solution. The rate constant of this reaction is measured by titrating a volume of the solution with a reducing agent which reacts only with B^{n+} and $B^{(n+4)+}$. In the process, it converts B^{n+} to $B^{(n+2)+}$ and $B^{(n+4)+}$ to $B^{(n-1)+}$. At $t = 0$, the volume of the reagent consumed is 25 mL and at $t = 10$ minutes, the volume used is 32 mL. The rate constant for the conversion of B^{n+} to $B^{(n+4)+}$ is found out in the form of $x \times 10^{-3}$. Find the value of x , assuming it to be a first order reaction.