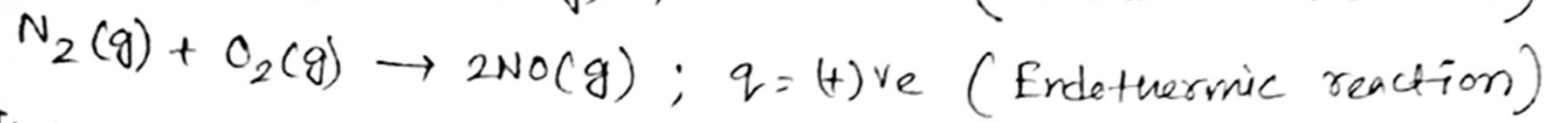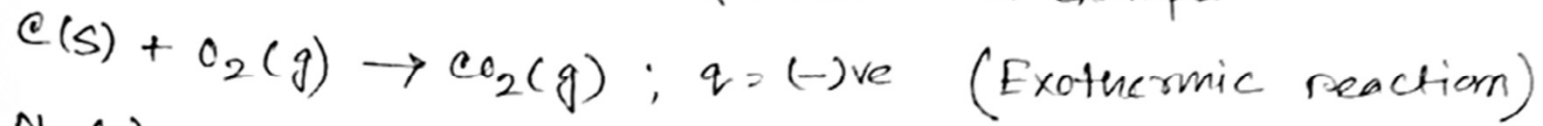# Lecture 6
Thermochemistry
&
Limitations of 1st Law of Thermodynamics

Thermochemistry

This chapter deals with the heat-change associated with a reaction. When heat is evolved, $q = \oplus$ ve and the reaction is called an Exothermic Reaction. and when heat is absorbed, $q = \ominus$ ve, the reaction is called an Endothermic Reaction. For example —

$$C(s) + O_2(g) \rightarrow CO_2(g) \; ; \; q = (-)ve \quad \text{(Exothermic reaction)}$$

$$N_2(g) + O_2(g) \rightarrow 2NO(g) \; ; \; q = (+)ve \quad \text{(Endothermic reaction)}$$

These heat-change occurs since a chemical reaction is associated with breaking of old bonds and making of new bonds. The subject matter of Thermochemistry is based on the 1st Law of Thermodynamics.

Heat of Reaction:

It is defined as the amount of heat change associated with a reaction as represented by the stoichiometric chemical equation. e.g. formation of $NO(g)$ is represented by — $N_2(g) + O_2(g) \rightarrow 2NO(g) \; ; \; q = 42 \; Kcal.$

But if the reaction is ~~an~~ represented as —

$$\tfrac{1}{2} N_2(g) + \tfrac{1}{2} O_2(g) \rightarrow NO(0) \;;\; q = 21 \text{ kcal}.$$
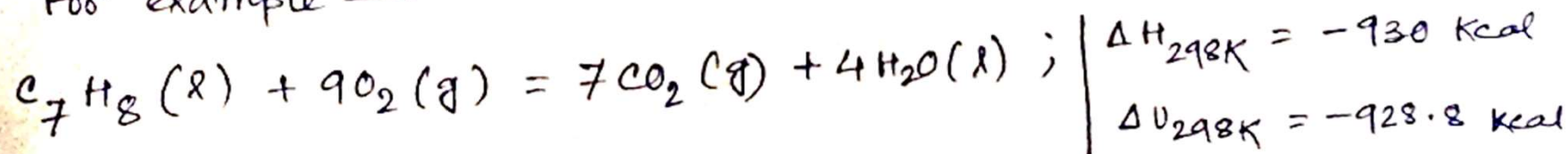
Heat of reaction is of two types.

1) Heat of reaction at constant pressure (q_P) and it is identified with Enthalpy change & Hence, $\boxed{q_P = \Delta H}$

2) Heat of reaction at constant volume (q_V) and it is identified with the change of internal energy i.e. $\boxed{q_V = \Delta U}$ $\boxed{\Delta H = \Delta U + \Delta n_g \cdot RT}$

further, Heat of reaction depends on temperature (T) and physical states of the reactants and products. When all these are included in one equatic it is called Thermochemical Equation.

for example —

$$C_7 H_8(\ell) + 9 O_2(g) = 7 CO_2(g) + 4 H_2O(\ell) \;;\; \left| \begin{array}{l} \Delta H_{298K} = -930 \text{ Kcal} \\ \Delta U_{298K} = -923.8 \text{ kcal} \end{array} \right.$$

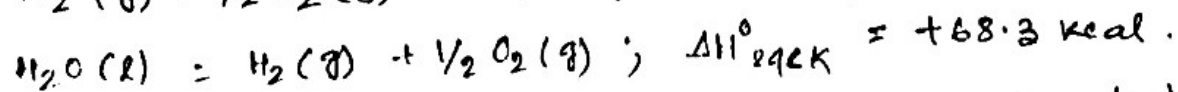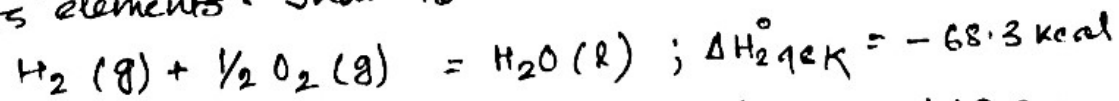## Standard Heat of reaction (ΔH^0):

When the reactants and products are in stable state of aggregration and at 1 atm pressure, the heat change in the reaction at constant pressure is called standard heat of reaction (ΔH^0).

☒ Laws of Thermochemistry: There are two laws —

1) Law of Lavoisier and Laplace:

the heat change accompanying a chemical reaction in one direction is equal in magnitude but opposite in sign to that accompanying the same react-ion in the reverse direction.

— Thus, Heat evolved in the formation of water (l) from $H_2(g)$ and $O_2(g)$ is exactly equal to the heat absorbed in the decomposition of waters into its elements. That is —

$$H_2(g) + \frac{1}{2}O_2(g) = H_2O(l) \; ; \; \Delta H^{\circ}_{298K} = -68.3 \, kcal$$

$$H_2O(l) = H_2(g) + \frac{1}{2}O_2(g) \; ; \; \Delta H^{\circ}_{298K} = +68.3 \, kcal.$$

— This Law is a consequence of 1st law of thermodynamics. 'H' is a state function and so it depends on the state of the system.

Let us suppose, the reactants A and B first change into the products C and D with heat change ΔH_1 and consequently when C & D

Table 2.4 Enthalpies of transition

Transition	Process	Symbol*
Transition	Phase $\alpha \rightarrow$ phase β	$\Delta_{trs}H$
Fusion	$s \rightarrow l$	$\Delta_{fus}H$
Vaporization	$l \rightarrow g$	$\Delta_{vap}H$
Sublimation	$s \rightarrow g$	$\Delta_{sub}H$
Mixing	Pure $\rightarrow$ mixture	$\Delta_{mix}H$
Solution	Solute $\rightarrow$ solution	$\Delta_{sol}H$
Hydration	$X^{\pm}(g) \rightarrow X^{\pm}(aq)$	$\Delta_{hyd}H$
Atomization	Species$(s, l, g) \rightarrow$ atoms(g)	$\Delta_{at}H$
Ionization	$X(g) \rightarrow X^{+}(g) + e^{-}(g)$	$\Delta_{ion}H$
Electron gain	$X(g) + e^{-}(g) \rightarrow X^{-}(g)$	$\Delta_{eg}H$
Reaction	Reactants $\rightarrow$ products	$\Delta_{r}H$
Combustion	Compound$(s, l, g) + O_2(g) \rightarrow CO_2(g), H_2O(l, g)$	$\Delta_{c}H$
Formation	Elements $\rightarrow$ compound	$\Delta_{f}H$
Activation	Reactants $\rightarrow$ activated complex	$\Delta^{\ddagger}H$

* IUPAC recommendations. In common usage, the transition subscript is often attached to ΔH, as in ΔH_{trs}.

2) **Hess's Law of constant Heat summation:**

Statement: "For a chemical reaction, the net heat change $(\Delta H \text{ or } \Delta U)$ will be same whether the process occurs in one step or in several steps.

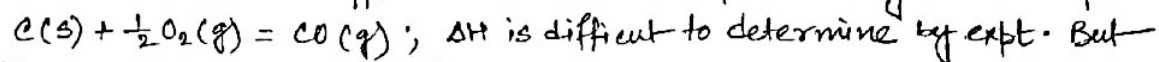**Illustration:** Let, a chemical reaction when occurs in one step —

$$A \rightarrow C \;;\; \Delta H = q_1$$
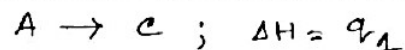
But when the same reaction occurs in two steps,

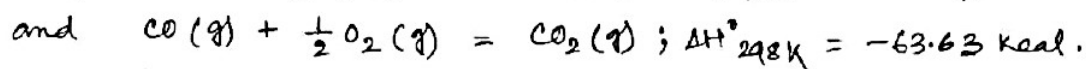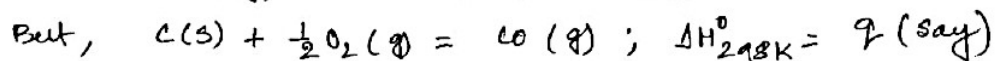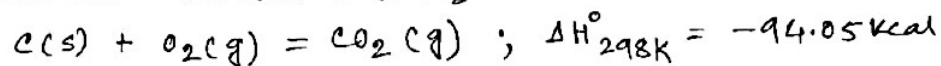$$A \rightarrow B \;;\; \Delta H = q_2 \;\&\; B \rightarrow C \;;\; \Delta H = q_3$$
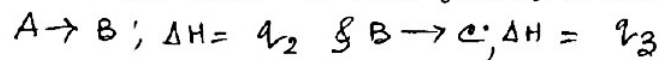
Then, according to the law, $\boxed{q_1 = q_2 + q_3}$ [This is also the consequence of 1st law of TD]

If the initial and final states of a process are fixed, the enthalpy change or Internal energy change will also be fixed and independent of the intermediate steps that occur.

This law is sometimes applied to calculate the heat change of some reactions which is difficult to determine experimentally. For example —

$$C(s) + \tfrac{1}{2}O_2(g) = CO(g) \;;\; \Delta H \text{ is difficult to determine by expt. But}$$

it can be calculated as follows: —

$$C(s) + O_2(g) = CO_2(g) \;;\; \Delta H^\circ_{298K} = -94.05 \, kcal$$

But, $\quad C(s) + \tfrac{1}{2}O_2(g) = CO(g) \;;\; \Delta H^\circ_{298K} = q \;(say)$

and $\quad CO(g) + \tfrac{1}{2}O_2(g) = CO_2(g) \;;\; \Delta H^\circ_{298K} = -63.63 \, kcal.$

Then, according to the law, $\quad (-94.05) = q + (-63.63)$

$$\boxed{q = -26.42 \, kcal}$$

·Kirchoff Equations: (dependence of heat of reaction on temperature)

If we know ΔH of a reaction at a given temp., then we can calcula the heat of reaction at another temp. provided the heat capacity of all the substances taking part in the reaction are known.

This equation can be derived as follows. If a system undergoes a. change from one state to another state, then $\Delta H = \left(H_f - H_i \right)$.

and $\Delta U = \left(U_f - U_i \right)$. Differentiating w.r.to 'T' at const. pressure for the former and at const. volume to the latter, then —

$$\left[\frac{\partial (\Delta H)}{\partial T} \right]_P = \left(\frac{\partial H_f}{\partial T} \right)_P - \left(\frac{\partial H_i}{\partial T} \right)_P = C_{P_f} - C_{P_i} \quad or \quad \left[\frac{\partial (\Delta H)}{\partial T} \right]_P = \Delta C_P$$

& the 2nd relation gives, $\left[\frac{\partial (\Delta U)}{\partial T} \right]_V = \Delta C_V$

here, C_{P_f} & C_{P_i} are the heat capacities of the final & initial states respe tive

Integrating within limits, we have, $\int_{\Delta H_1}^{\Delta H_2} d(\Delta H) = \int_{T_1}^{T_2} \Delta C_p \cdot dT$

or, $\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_p \, dT$ —①

and the other relation is, $\Delta U_2 - \Delta U_1 = \int_{T_1}^{T_2} \Delta C_V \, dT$ —②

Two cases may arise —

(1) when, Δc_p is independent of temp $\stackrel{r}{\cdot}$, $\Delta H_2 = \Delta H_1 + \Delta c_p (T_2 - T_1)$ —③

& when Δc_v is also independent & $\Delta U_2 = \Delta U_1 + \Delta c_v (T_2 - T_1)$ —④
of temp $\stackrel{r}{\cdot}$.

(2) When, Δc_p is dependent of temp $\stackrel{r}{\cdot}$, Δc_p has to be expressed as function of T as by the use of virial equation—

Let, $c_p = a + bT + cT^2 + \cdots$ when $a, b, c \cdots$ are called virial coefficient.

These coefficients depend on the nature of substance only.

$$\Delta c_p = c_{p_f} - c_{p_i} = (a_f - a_i) + (b_f - b_i)T + (c_f - c_i)T^2 + \cdots$$

$$= \Delta a + \Delta b \cdot T + \Delta c \cdot T^2 + \cdots$$

or, $\Delta c_p = \alpha + \beta T + \gamma T^2 + \cdots$ putting these virial form of Δc_p,

We get, $\Delta H_2 = \Delta H_1 + \displaystyle\int_{T_1}^{T_2} (\alpha + \beta T + \gamma T^2 + \cdots) dT$
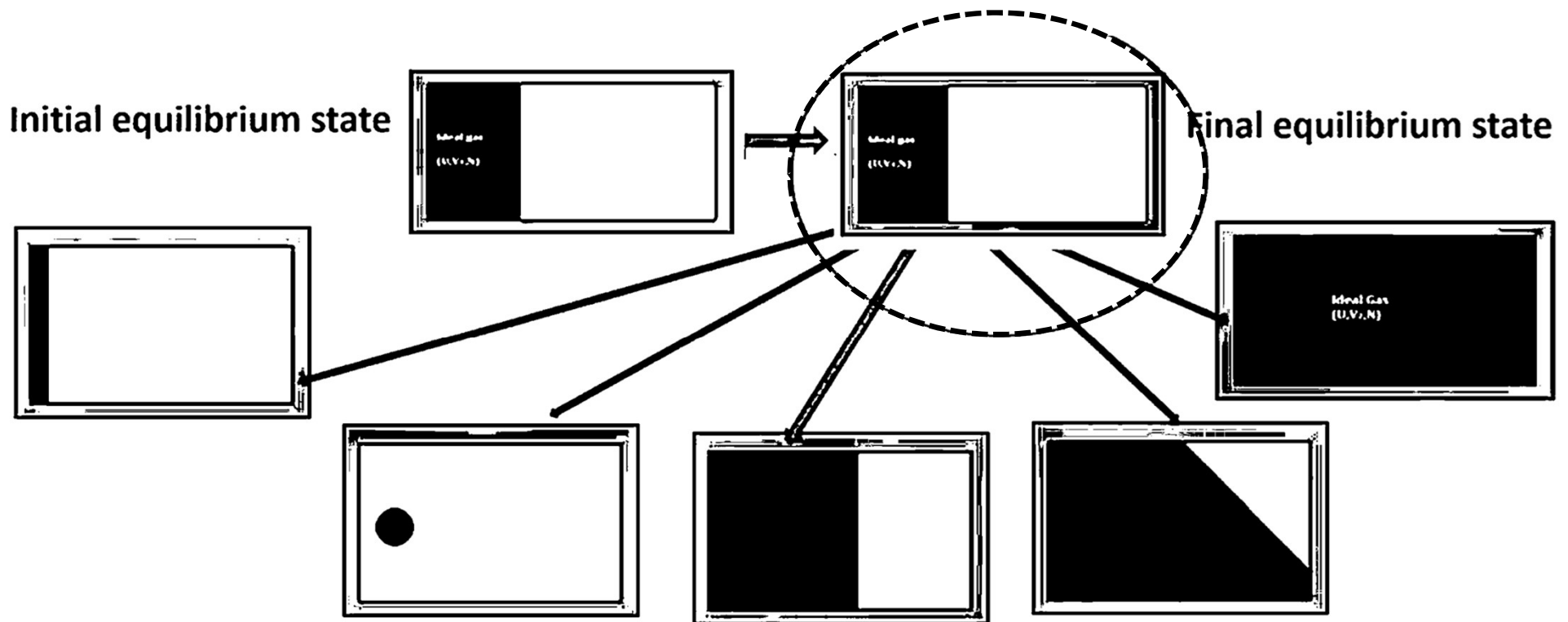
$\therefore$ or, $\Delta H_2 = \Delta H_1 + \alpha(T_2 - T_1) + \dfrac{\beta}{2}(T_2^2 - T_1^2) + \dfrac{\gamma}{3}(T_2^3 - T_1^3) + \cdots$ ⑤

The other equation is —

$$\Delta U_2 = \Delta U_1 + \alpha'(T_2 - T_1) + \dfrac{\beta'}{2}(T_2^2 - T_1^2) + \dfrac{\gamma'}{3}(T_2^3 - T_1^3) + \cdots$$

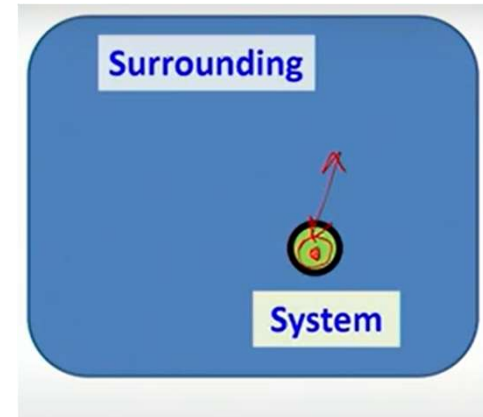These equations from ① to ⑥ are the different forms of Kirchoff Equation .

Thermodynamics- Part II

Initial equilibrium state

Final equilibrium state

1st Law and Its Limitations

- The concept of **internal energy, *U*** and **enthalpy, *H***

- **Assumption:**

  ✓ Universe: **system + surrounding**
  ✓ Universe is **isolated**

- During any **change in state of the system**

1st law states that if due to heat flow, q amount of heat is lost by A then exactly q amount of heat will be gained by B

Surrounding

System

The perfect heat engine

Efficiency of the heat engine

$$\eta = \frac{|w|}{Q_h}$$

1st law predicts that construction of such an engine is possible

Limitations of 1st Law

➤ Whether heat-flow or such change in state would occur or not ?
➤ If the heat flow/ change in state occurs what will be the spontaneous direction?
➤ What will be the new equilibrium state and under which condition will the change stop ?

- From the 1st law, when $\Delta U = 0$, $q = -w$.
  So heat supplied to a system can be **completely** converted to work!!

- Such possibility is tested by the construction of **heat engines**