Chapter III :

Thermochemistry

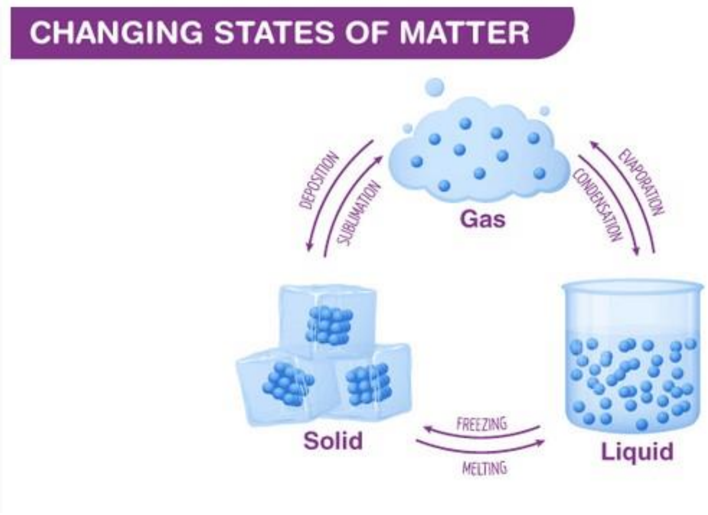
I- Introduction :

Thermochemistry is the study of the heat energy which is associated with chemical reactions and/or phase changes such as melting and boiling. A reaction may release or absorb energy, and a phase change may do the same.

II- Changing State :

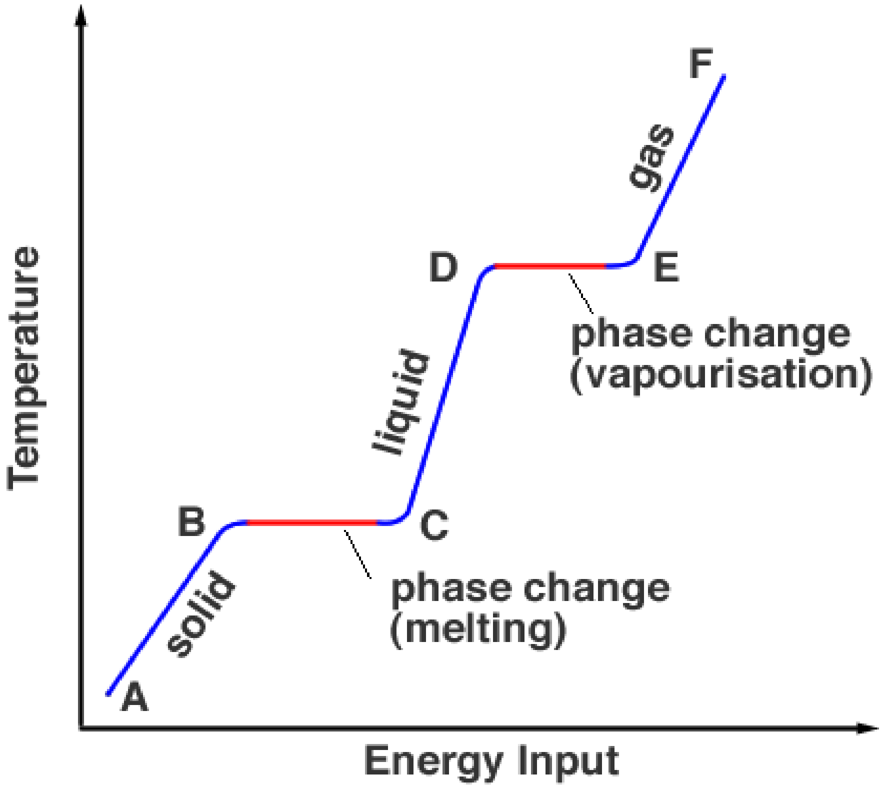
Changing state is the term used to describe the process of one state of matter (solid, liquid or gas) changing to another. An everyday example of this is ice melting. This is a solid (ice) changing state to become liquid (water). States of matter change when their particles either gain or lose energy; this can be due to a change in temperature. If it gets warmer, particles gain energy; if it gets colder, they lose energy. The important thing to remember is matter cannot be destroyed; it can only change. There are six changes of state possible between solids, liquids and gases:

- **Melting** is when a solid changes to a liquid.
- **Freezing** is when a liquid changes to a solid.
- **Evaporation** (or vapourisation) is when a liquid changes to a gas.
- **Condensation** is when a gas changes to a liquid.
- **Sublimation** is when a solid changes to a gas.
- **Deposition** is when a gas changes to a solid.



When a substance changes phase, that is it goes from either a solid to a liquid or liquid to gas, the energy, it requires energy to do so. The potential energy stored in the interatomics forces between molecules needs to be overcome by the kinetic energy the motion of the particles before the substance can change phase.

Continuous heating of pure solid results in transformations represented in the following scheme:



Starting a point *A*, the substance is in its solid phase, heating it brings the temperature up to its melting point but the material is still a solid at point *B*. As it is heated further, the energy from the heat source goes into breaking the bonds holding the atoms in place. This takes place from *B* to *C*. At point *C* all of the solid phase has been transformed into the liquid phase. Once again, as energy is added the energy goes into the kinetic energy of the particles raising the temperature, (*C* to *D*). At point *D* the temperature has reached its boiling point but it is still in the liquid phase. From points *D* to *E* thermal energy is overcoming the bonds and the particles have enough kinetic energy to escape from the liquid. The substance is entering the gas phase. Beyond *E*, further heating under pressure can raise the temperature still further is how a pressure cooker works.

III- Relation to internal energy variation :

The following relation can be established between the standard enthalpy of a reaction and the variation in standard internal energy:

$$aA_{(g)} + bB_{(g)} \quad \rightarrow \quad cC_{(g)} + dD_{(g)}$$

$$P_1, V_1, T, \quad n_1 = a + b \qquad\qquad P_2, V_2, T, \quad n_2 = c + d$$

$$U_1, \ H_1 \qquad\qquad U_2, \ H_2$$

$\Delta H = H_2 - H_1 = (U_2 + P_2V_2) - (U_1 + P_1V_1)$

$\Delta H = \Delta U + (P_2V_2 - P_1V_1)$

We have : $P_1V_1 = n_1RT$, $P_2V_2 = n_2RT$

Compensation in the previous equation we find :

$\Delta H = \Delta U + (n_2RT - n_1RT)$

$$\mathbf{\Delta H = \Delta U + \Delta n_{gRT}}$$

Δn_g calculated only for gaseous materials.

IV- Heat of a reaction :

we have the next chemical reaction :

$$\boldsymbol{aA + bB} \quad \rightarrow \quad \boldsymbol{cC + dD}$$

Reactants products

Heat of a reaction is defined as the amount of heat absorbed or evolved at a given temperature when the reactants have combined to form the products is represented by balanced chemical equation.

When the reaction evolves energy in the form of heat, it called exothermic reaction and When the reactants absorb heat energy from the surroundings to form products, the reaction called endothermic reaction.

- If the reaction happens at constant volume, the heat of the reaction called constant volume heat Q_V.

$$\mathbf{Q_V = \Delta U}$$

This quantity (ΔU), called the change in internal energy of reaction, is the heat of reaction at constant volume.

- If the reaction occurs at constant pressure, the heat of the reaction called heat at constant pressure Q_P.

$$\mathbf{Q_P = \Delta H}$$

This quantity (ΔH), called the change in enthalpy of reaction, is the heat of reaction at constant pressure.

V- Enthalpy of Reaction

a. Definition :

The **enthalpy of reaction (ΔH_R)** is the change in enthalpy due to a chemical reaction.

If $\Delta H_R > 0$, the reaction is **endothermic** (the system pulls in heat from its surroundings)

If $\Delta H_R < 0$, the reaction is **exothermic** (the system releases heat into its surroundings).

b. Latent heat :

latent heat, energy absorbed or released by a substance during a change in its physical state (phase) that occurs without changing its temperature. The latent heat associated with melting a solid or freezing a liquid is called the heat of fusion; that associated with vaporizing a liquid or a solid or condensing a vapour is called the heat of vaporization. The latent heat is normally expressed as the amount of heat (in units of joules or calories) per mole or unit mass of the substance undergoing a change of state.

For example, when a pot of water is kept boiling, the temperature remains at 100 °C (212 °F) until the last drop evaporates, because all the heat being added to the liquid is absorbed as latent heat of vaporization and carried away by the escaping vapour molecules. Similarly, while ice melts, it remains at 0 °C (32 °F), and the liquid water that is formed with the latent heat of fusion is also at 0 °C. The heat of fusion for water at 0 °C is approximately 334 joules (79.7 calories) per gram, and the heat of vaporization at 100 °C is about 2,230 joules (533 calories) per gram. Because the heat of vaporization is so large, steam carries a great deal of thermal energy that is released when it condenses, making water an excellent working fluid for heat engines.

- **Enthalpy of fusion (ΔH_{fus}) (or Latent Heat of fusion):** change in enthalpy due to fusion (melting) of 1 mol of a substance.
- **Enthalpy of vaporization (ΔH_{vap}) (or Latent Heat of vaporization):** change in enthalpy due to vaporizing (liquid to gas) of 1 mol of a substance.
- **Enthalpy of condensation (ΔH_{cond}) (or Latent Heat of condensation):** change in enthalpy due to condensation of 1 mol of a substance, condensation is the polar opposite of evaporation.

$$\Delta H_{cond} = - \Delta H_{vap}$$

- **Enthalpy of solidification (ΔH_{solid}) (or Latent Heat of solidification):** change in enthalpy due to solidification **(**freezing**)** of 1 mol of a substance.

$$\Delta H_{solid} = - \Delta H_{fus}$$

c. standard enthalpy of formation:

The standard enthalpy of formation of a substance is the enthalpy change that occurs when 1 mole of the substance is formed from its constituent elements in their standard states. A pure element in its standard state has a standard enthalpy of formation of zero.

- **The Standard States of Elements :**

The standard states of elements are the forms that they adopt at a temperature of 25°C and pressure of 1 atmosphere (1 atm).

These forms of the elements are the reactants in the formation equations of multi-element substances.

Please note that some elements have multiple possible forms at the standard state such as carbon, which can be either graphite or diamond. However only one of these forms is the true standard state; in those cases the proper state will be listed next to the formula for the element.

Gases

• Hydrogen H_2(g), Nitrogen N_2(g), Oxygen O_2(g), Fluorine F_2(g), Chlorine Cl_2(g)…

Liquids

• Bromine Br_2(l), Mercury Hg(l)…

Solids

Carbon C(s) – graphite, Sodium Na(s), Silver Ag(s)…

The standard <u>enthalpy of formation</u> ($\Delta H_f°$) is the enthalpy change for the formation of 1 mol of a compound from its elements. These elements are in their standard state, which is the most stable form of the element at 1 atm and 298 K. Here is an example:

$$C + O2 \rightarrow CO2 \quad \Delta H°_f = -393.5 \text{ kJ/mol}$$

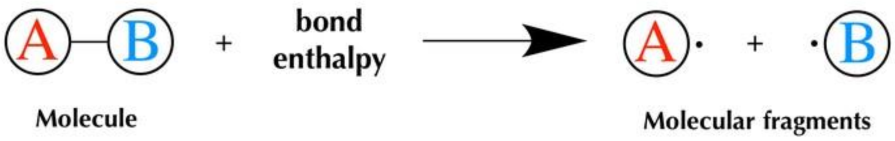
Here is a table of some common standard enthalpies of formation:

Compound	$\Delta H°_f$ (kJ/mol)
$CO_{(g)}$	-393.5
$H_2O_{(g)}$	-241.8
$H_2O_{(l)}$	-285.8
$NaCl_{(s)}$	-411.0
$NH_{3\,(g)}$	-46.2
$NO_{2\,(g)}$	33.9

The standard enthalpy is dependent on the state (ex: solid/liquid/gas) of the molecule. As you'll see above, the standard enthalpy for water as a liquid and as a gas is different. In addition, The heat of formation ($\Delta H_f°$) of an element in its standard state is zero. This is because it doesn't take any energy to form a naturally occurring compound (there is no reaction).

d. Bond enthalpy :

Bond enthalpy (which is also known as bond-dissociation enthalpy, average bond energy, or bond strength) describes the amount of energy stored in a bond between atoms in a molecule. Specifically, it's the energy that needs to be added for the homolytic or symmetrical cleavage of a bond in the gas phase. A homolytic or symmetrical bond breaking event means that when the bond is broken, each atom that originally participated in the bond gets one electron and becomes a radical, as opposed to forming an ion.



- **Bond Energy :**

No molecule within chemistry would exist without bonds linking atoms. Because forming bonds releases energy, molecules exist because atoms prefer a stable compound with less energy. In order to break these stable bonds, energy must be added to the system. Thus, this value is known as bond energy.

Energy is always required when breaking a bonds as an endothermic reaction. On the other hand, energy is always released when forming bonds as an exothermic reaction.

Bond energies, or the strength of a bond, determine how much energy is released or required in these processes. Molecules can differ in their overall reaction enthalpies depending on its bonds.

- **Bond Formation and Dissociation Energies :**

A molecule's bond formation energy is the heat/energy released when forming the product. In a reaction, the bond formation energy is the energy released in the product-forming step. Consequently, this value is always negative as forming bonds release energy.

A molecule's bond dissociation energy is the heat required to break bonds. In a reaction, the bond dissociation energy is the energy required to break apart the original reactant's bonds. Consequently, this value is always positive as breaking bonds require energy.

Adding the dissociation and formation energies results in the overall enthalpy of reaction, or the net total of energy throughout the reaction's progress. Thus, bond formation and dissociation energies determine whether an overall reaction's enthalpy is endothermic or exothermic.

If breaking the reactant's bonds require more energy than the energy released in the product's formation, the reaction is endothermic. If a product's formation releases more energy than breaking the reactant's bonds, the reaction is exothermic.

Tip: The bond values listed in tables are for a mole of reaction for a single bond. This means that if there are multiples of the same bond breaking or forming in a reaction, you will need to multiply the bond enthalpy in your calculation by how many of that type of bond you have in the reaction. This also means it's important to make sure the equation is balanced and that the coefficients are written as the smallest possible integer values so the correct number of each bond is used.

VI- Measurement of Enthalpy of chemical reaction :

a- direct method :

The experimental technique known as calorimetry is used to assess enthalpy and internal energy in most cases. Calorimetry is based on thermometric methods that are carried out in a calorimeter that is immersed in a known volume of liquid. The heat released during the process is typically computed using known heat capacities of the liquid and temperature changes measured by the calorimeter.

b- Indirect method :

Hess’s law :

Hess’s law, rule first enunciated by Germain Henri Hess, a Swiss-born Russian chemist, in 1840, stating that the heat absorbed or evolved (or the change in enthalpy) in any chemical reaction is a fixed quantity and is independent of the path of the reaction or the number of steps taken to obtain the reaction. Hess’s law can be written as $\Delta H° = \Sigma\Delta H_n$, where $\Delta H°$ is the heat absorbed or evolved and $\Sigma\Delta H_n$ is the sum of the heat absorbed or evolved in the individual *n* steps of the reaction. Hess’s law is a consequence of the first law of thermodynamics and need not be considered a separate thermodynamic law; in thermochemistry, however, it retains its identity because of its importance as the basis for calculating heats of reactions. Hess’s law is exemplified by the calculation of the heat of formation of carbon dioxide from its elements (carbon [C] and oxygen [O]). This reaction is represented by

$$C(c) + O_2(g) \longrightarrow CO_2(g);$$
$$\Delta H° = -94.054 \text{ kcal (kilocalorie)}$$

In the equation (c) and (g) denote crystalline and gaseous, respectively; here $\Delta H°$ is called the heat of formation.

In accordance with Hess’s law, the heat of formation of carbon dioxide is the same, whether it occurs in one reaction as represented by the equation above or in two steps as represented by the equations given below:

$$C(c) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g);$$
$$\Delta H° = -26.417 \text{ kcal}$$
$$CO(g) + \tfrac{1}{2}O_2 \longrightarrow CO_2(g);$$
$$\Delta H° = -67.637 \text{ kcal}$$

The sum of the above equations is:

$$C(c) + O_2(g) \longrightarrow CO_2(g);$$
$$\Delta H° = -94.054 \text{ kcal.}$$

Thus Hess’s law allows the calculation of the heats of various reactions from the heats of other reactions.

b-1. Using enthalpy of formation to estimate enthalpy of reaction :

When we calculate the reaction enthalpy using standard enthalpies, then it is the standard reaction enthalpy.

Now that we have a basic understanding of reaction enthalpy, let's learn how to calculate it. There are a few "rules" to follow when looking at enthalpy change.

First: when a reaction/process is reversed, the sign of the reaction enthalpy changes. For example, when ice melts, the reaction has a positive enthalpy change (it is absorbing heat to melt). However, when water freezes, the enthalpy change is negative since it is releasing heat (it is cooling).

Second: enthalpy is proportional to the amount of reactants. When you look up enthalpy values for reactions, it is assumed that it is for 1 mol of reactants. So if you wanted to know the ΔH_{rxn} for 3 mols of reactant, then you would multiply the given value by three.

Example: Calculate $\Delta H_R°$ for the following reaction:

$$NH_{3(g)} + HCl_{(g)} \rightarrow NH_4Cl_{(S)}$$

We have :

$$\Delta H°_{f(NH_{3(g)})} = -46{,}9\ KJ.mol^{-1},\ \Delta H°_{f(HCl_{(g)})} = -92{,}3\ KJ.mol^{-1}$$

$$\Delta H°_{f\left(NH_4Cl_{(S)}\right)} = -314{,}4\ KJ.mol^{-1}$$

According to the Hess law:

$$\begin{tikzcd}
NH_{3(g)} + HCl_{(g)} \arrow[rr, "\Delta H°_R"] & & NH_4Cl_{(S)} \\
& \frac{1}{2}\ N_{2(g)} + 2\ H_{2(g)} + \frac{1}{2}\ Cl_{2(g)} \arrow[ul, "\Delta H°_{f(NH_{3(g)})} + \Delta H°_{f(HCl_{(g)})}"] \arrow[ur, "\Delta H°_{f\left(NH_4Cl_{(S)}\right)}"'] &
\end{tikzcd}$$

$$\Delta H°_R = \Delta H°_{f\left(NH_4Cl_{(S)}\right)} - \left[\Delta H°_{f(NH_{3(g)})} + \Delta H°_{f(HCl_{(g)})}\right]$$

$$\Delta H°_R = -314{,}4 - (-46{,}9 - 92{,}3) = -175{,}2\ \mathrm{KJ}$$

This includes, in general, all reactions:

Enthalpy of chemical reaction is equal to the total standard enthalpy of formation of products minus the total standard enthalpy of formation of reactants.

$$\Delta H°_R = \sum n_p \left(\Delta H°_f\right)_p - \sum n_R \left(\Delta H°_f\right)_R$$

$$aA + bB \xrightarrow{\Delta H°_R} cC + dD$$

$$\Delta H°_R = \left[c\, \Delta H°_{f(C)} + d\, \Delta H°_{f(D)}\right] - \left[a\, \Delta H°_{f(A)} + b\, \Delta H°_{f(B)}\right]$$

b-2. Using bond enthalpies to estimate enthalpy of reaction :

Once we understand bond enthalpies, we use them to estimate the enthalpy of reaction. To do this, we can use the following procedure:

Step 1. Identify which bonds in the reactants will break and find their bond enthalpies.

Step 2. Add up the bond enthalpy values for the broken bonds.

Step 3. Identify which new bonds form in the products and list their negative bond enthalpies. Remember we have to switch the sign for the bond enthalpy values to find the energy released when the bond forms.

Step 4. Add up the bond enthalpy values for the formed product bonds.

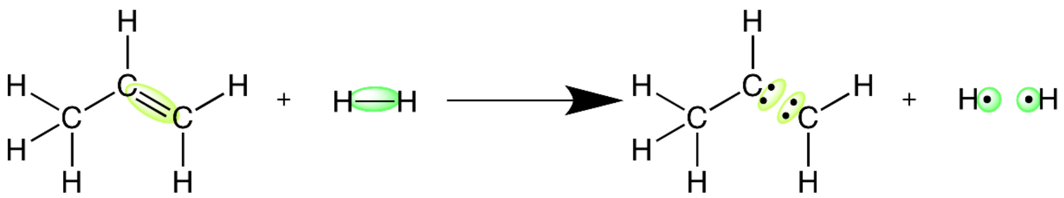
Step 5. Combine the total values for breaking bonds (from **Step 2**) and forming bonds (from **Step 4**) to get the enthalpy of reaction.

Example: Hydrogenation of propene :

Let's find the enthalpy of reaction for the hydrogenation of propene, our example from the beginning of the article.

Step 1: Identify bonds broken

This reaction breaks one C=C bond and one H-H bond.



Using a reference table, we find that the bond enthalpy of a C=C bond is 610KJ/mol , while the bond enthalpy of a H-H bond is 436KJ/mol.

Step 2: Find total energy to break bonds

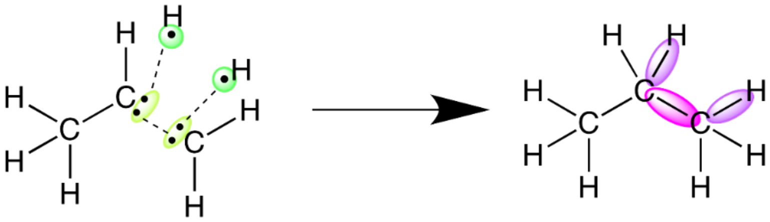
Combining the values from **Step 1** gives us:

Energy added to break bonds = 610 KJ/mol + 436 KJ/mol=1046 KJ/mol

as the total energy required to break the necessary bonds in propene and hydrogen gas.

Step 3: Identify bonds formed

This reaction forms one new C-C bond and two new C-H bonds.



Using a reference table, we find that the bond enthalpy of a C-C bond is 346 KJ/mol , while the bond enthalpy of a C-H bond is 413KJ/mol. To find how much energy is released when these bonds are formed, we'll need to multiply each bond enthalpy by -1 . Also, since *two* new C-H bonds are formed, we'll need to multiply the C-H bond enthalpy by 2.

Step 4: Find total energy released to form new bonds

Combining the values from **Step 3** gives us:

Energy released to make product bonds = -346 KJ/mol + 2(-413 KJ/mol) =

-1172 KJ/mol

for the total energy that will be released by forming the new bonds.

Step 5: Add up energy for bonds broken and formed

From **Step 2** and **Step 4**, we have 1046 KJ of energy required to break bonds and -1172 KJ of energy released from forming bonds. Combining these values, we get for the enthalpy of reaction:

ΔH_R = energy added to break reactant bonds + energy released when making product bonds

= 1046 KJ/mol + (-1172 KJ/mol)

= - 126 KJ/mol

Since the enthalpy of reaction for the hydrogenation of propene is negative, we know that the reaction is exothermic.

Summary :

Bond enthalpy and enthalpy of reaction help us understand how a chemical system uses energy during reactions. The bond enthalpy describes how much energy is needed to break or form a bond, and it is also a measure of bond strength. By combining the bond enthalpy values for all of the bonds broken and formed during a reaction, it's possible to estimate the total change in potential energy of the system, which is ΔH_R for a reaction at constant pressure. Depending on whether the enthalpy of reaction is positive or negative, we can determine whether a reaction will be endothermic or exothermic.

VII- Effect of Temperature on Heat of Reaction: (The Kirchhoff Equation)

KIRCHHOFF's law involves determining the enthalpy of reaction at a temperature different from that of the standard state.

Kirchhoff's Equation is equality expressing the temperature dependence of the thermal quantities linked with a chemical reaction through the difference in heat capacities between the products and reactants. The same reaction, when carried at dissimilar temperatures, the enthalpies of reaction are also different.

we have the next chemical reaction :

$$aA + bB \rightarrow cC + dD$$

$$\Delta H_R = \sum n_p \left(\Delta H°_f\right)_p - \sum n_R \left(\Delta H°_f\right)_R$$

$$\Delta H_R = d\Delta H(D) + c\Delta H(C) - a\Delta H(A) - b\Delta H(B)$$

We know that :

$$C_P = \left(\frac{d\Delta H}{dT}\right)_p$$

By deriving the previous equation for T:

$$\frac{d\Delta H_R}{dT} = \frac{d}{dT}\left[\sum n_p\,(\Delta H)_p - \sum n_R\,(\Delta H)_R\right]$$

$$= \sum n_P\, C_{P(produits)} - \sum n_R\, C_{P(réactifs)}$$

$$\frac{d\Delta H_R}{dT} = \Delta n C_P \dots\dots\dots..(1)$$

$$\Delta n C_P = dC_P(D) + cC_P(C) - aC_P(A) - bC_P(B)$$

By integrating relationship (1) we find:

$$\int_{\Delta H_{T_0}}^{\Delta H_T} d\,(\Delta H_R) = \int_{T_0}^{T} \Delta n C_P\, dT$$

$$\Delta H_T = \Delta H_{T_0} + \int_{T_0}^{T} \Delta n C_P\, dT$$

Similarly, it may be shown that if the process is carried out at constant volume the relationship is :

$$\Delta U_T = \Delta U_{T_0} + \int_{T_0}^{T} \Delta n C_V\, dT$$