Boyle's Law

At constant temperature, the volume of a definite mass of gas is inversely proportional to the pressure i.e. at fixed temperature, the product of the pressure ($P$) and volume ($V$) of a given mass of gas is constant.

This can be written in the form of the equation:

$$ V \propto \frac{1}{P} \quad \text{(At constant temp.)} $$

$$ V = \frac{K}{P} $$

where, $P = \text{pressure}$, $V = \text{volume of a definite mass of gas at constant temp.}$

or

$$ PV = K \quad \ldots \quad (1) $$

where $K = \text{constant}$, its magnitude depends on temp. and mass of the gas and also upon its nature.

Boyle's law can be expressed in another manner:

$$ P_1 \cdot V_1 = P_2 \cdot V_2 \quad \ldots \quad (2) $$

$V_1 = \text{volume of a given mass of gas when the pressure is } P_1$

$V_2 = \text{the same mass of gas when the pressure is changed to } P_2 \text{ at the same temperature.}$
Example: A given mass of gas occupies a volume of 240 ml at pressure of 1.25 atm. By how much would the volume change if the pressure were altered to 0.75 atm at the same temperature?

If we plot the pressure as ordinates and the volume (at const. temp) as abscissae, we obtain Figure (1). The curve is rectangular hyperbola.

![Figure 1 - Isotherm for ideal gas](image)

The curve is described as Isotherm

I**sotherm** = Variation of volume with pressure at constant temperature.

As shown in Fig (1), for each temp a different curve (hyperbola) is obtained.
لا يمكن قراءة النص العربي من الصورة.
Gay-Lussac's Law or Charles-Law

Charles Law

At constant pressure ($P$), the volume of a fixed mass of any gas increases by the same relative amount (or fraction) for any degree rise in temperature.

or The volume increases linearly with temperature.

\[ V \propto T \quad \text{(at constant $P$)} \]
\[ V = kT \quad \ldots \quad (3) \]

The linear variation of volume ($V$) with temperature is illustrated in Fig.(2).

(2) Gay-Lussac's Law isobars for an ideal gas

\[ \frac{V_1}{T_1} = \frac{V_2}{T_2} = \text{constant} \quad \text{(at const. press)} \]
\[ \frac{V_1}{V_2} = \frac{T_1}{T_2} \quad \left( \frac{V_1}{V_2} = \text{constant} \right) \]
Charles' Law

Any gaseous substance can be represented as:

The volume of a given mass of a gas at a definite pressure is directly proportional to the absolute temp (T).

The straight lines in Fig (1) called isobars (constant pressure) which extrapolates to zero volume at 0°C.

Example: The volume of a given mass of gas is 360 ml at 15°C. At what temp will the volume be 480 ml? Assuming constant pressure.

Equation of State (قانون مادت

The expression which represents the relationship between the pressure (P), volume (V), and temperature (T) of a given mass of gas.

Suppose the gas has initially a volume V₁ at press. P₁ and temp. T₁. Then when the pressure is changed to P₂ and the temp to T₂, the volume will be V₂.

Suppose the temp is maintained constant at T₁ while the press. is changed from P₁ to P₂ and the volume is changed from V₁ to V₂.

Then Boyle's equation becomes:

$$ P₁ V₁ = P₂ V₂ \quad \text{(Fixed temp T₁)} $$
2. Now the pressure is kept constant at $P_2$ and the temp. is altered from $T_1$ to $T_2$. The volume will change from $V_1$ to $V_2$. Applying **Charles' law** equation at const. press.: \[
\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \text{(2)}
\]
Introducing the value of $V_1$ in equation (2):
\[
\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad \text{(3)}
\]
Similar results can be obtained for the volume $V_3$ at press. $P_3$ and temp. $T_3$:
\[
\frac{P_3 V_3}{T_3} = \frac{P_2 V_2}{T_2} = \frac{P_1 V_1}{T_1} \quad \text{etc.} \quad \text{(4)}
\]
In general \[
\frac{P V}{T} = \text{Constant} \quad \text{(for a given mass of gas)}
\]
For a definite mass of gas, any change of $T$ and $P$ will be accompanied by an adjustment of $V$ so that the quantity $\frac{P V}{T}$ = const = $R$. (Refer: continue on page 78).

Example. A given mass of a gas occupies a volume of 250 ml at 21°C and a pressure of 1.40 atm. What pressure will the volume be 300 ml when the temp. is raised to 49°C?
Gay-Lussac's Law:

**Dependence of pressure on temperature.**

If the volume of a fixed mass of gas is maintained constant (\(V = \text{constant}\)), then

\[
P \propto \frac{1}{T}
\]

or

The pressure of a given mass of gas at constant volume is directly proportional to the absolute temperature.

\[\text{Gay-Lussac}\]

\[\text{Graph: } P \propto T^{\frac{1}{2}}\]

**Why the pressure depends on temp??**

The explanation is that raising the temperature of a gas increases the average speed of its molecules. The molecules collide with the walls more frequently and do so with greater impact. Therefore they create a greater pressure on the walls of the container.

The variation of the volume or pressure of a fixed mass of gas as a function of temperature (\(V, P \propto T\)) forms the basis of the system of temp measurement (e.g. in gas thermometers with He-gas).

Now, mercury 'Hg' in glass thermometers are used. These are calibrated under ordinary atmospheric conditions at sea level (i.e.) 760 mm at 0°C.
The height of the column of Hg above the lower Hg surface represents the pressure (measured as force per unit area exerted by earth's atmosphere $\frac{F}{A}$).

**Avogadro's Law**

Equal volumes of gases at the same pressure and temperature contain the same number of molecules (i.e. at constant $P$ and $T$) of any substance at the same $P$ and $T$ always contain the same number of molecules.

Hence, for 1 mole of gas, $\frac{PV}{T}$ will be equal to universal constant ($R$) known as the gas constant.

The ideal gas equation (The combined gas law) According to Boyle's, Charles', Gay-Lussac and Avogadro laws, the general equation of state of any gas would be:

$$\frac{PV}{T} = \text{constant} = R \quad \ldots \ (1)$$

where, $V =$ The volume occupied by 1 mole (Molar volume) at press $P$ and Temp. $T$.

The volume of $n$ moles should be $n$ times as great as for 1 mole.
If \( V_n \) is the volume for \( n \) moles, then:

\[
P V_n = nRT \quad \text{(Ideal gas equation)} \quad (2)
\]

This is called the perfect or ideal gas equation.

The constant \( R \) is called the gas constant, it is the same for all gases.

The equation of state (2) is consistent with Boyle's law \( (P V = \text{constant}) \) and Charles', Gay-Lussac's laws \( (P_2 V = T_2) \) and Avogadro's principle \( (V = n) \) when \( P, T \) are constants.

The ideal or perfect gas is the gas to which the laws of Boyle and Gay-Lussac are strictly applicable. Equation (2) is the approximate equation of state of any gas and becomes increasingly exact when the pressure of the gas approaches zero \( (P \to 0) \).

\[
\begin{align*}
P & \quad \text{const} (T) \quad \text{const} (P) \quad \text{const} (V) \\
V & \quad \text{const} (P) \quad \text{const} (T) \quad \text{const} (T)
\end{align*}
\]

To correct for departure from ideal behavior:

- Measuring the volumes of gases at different pressures and constant temp. and extrapolating the data to zero pressure.

The volume of any gas should extrapolate to zero at \( T = -273^\circ C \) and therefore \( (-273^\circ C) \) is a natural
Zero of a temp scale (Celsius). The thermodynamic temp. scale devised by Kelvin is (T=0°C + 273)

Also, 1 mole of an ideal gas at standard temp and press (S.T.P) defined as T=0°C or 273 K and 1 atm (760 mm mercury) is 22.414 liters.

Example Using the perfect gas equation

In an industrial process, nitrogen is heated to 500 K in a vessel of constant volume. If it enters the vessel at a pressure of 100 atm and a temp. of 300 K. What pressure would it exert at the working temp. if it behaved as a perfect gas?

<table>
<thead>
<tr>
<th>P</th>
<th>V</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td>Const</td>
<td>100</td>
<td>Const.</td>
</tr>
<tr>
<td>Const</td>
<td>?</td>
<td>Const.</td>
</tr>
</tbody>
</table>

Mixture of gases

Dalton's Law of Partial pressures:

The total pressure of a mixture of gases is equal to the sum of the partial pressures of the constituent gases.

The partial pressure of each gas in a mixture is defined as the pressure the gas would exert
if it alone occupied the whole volume of the mixture at the same temperature.

A vessel of volume \( V \) containing three gases, the amounts being \( n_1 \), \( n_2 \), and \( n_3 \) moles respectively. Suppose the vessel is occupied exclusively by

\( n_1 \) moles of the first gas, the pressure would be \( P_1 \).

If the vessel contained the \( n_2 \) moles of the second gas only, the pressure would be \( P_2 \).

If the \( n_3 \) moles of the third gas are the sole occupants of the vessel, the pressure would be \( P_3 \).

All at a definite temperature \((T=\text{const.})\).

By the law of partial pressures:

\[ P = P_1 + P_2 + P_3 + \ldots \text{ etc} \quad \ldots \quad (1) \]

\( P = \text{Total pressure when the three gases are present in the vessel.} \)

And so on for any mixture of gases.

When the gases separately occupy the vessel of volume \( V \), then equation of state for each gas is:

\[ P_1 V = n_1 RT \quad \ldots \quad 2(a) \]

\[ P_2 V = n_2 RT \quad \ldots \quad 2(b) \]

\[ P_3 V = n_3 RT \quad \ldots \quad 2(c) \]
\[(P_1 + P_2 + P_3 + \ldots) V = (n_1 + n_2 + n_3 + \ldots) RT \ldots (3)\]

Substituting eq. (4):

\[PV = (n_1 + n_2 + n_3 + \ldots) RT = \pi RT \ldots (4)\]

where, \(\pi = n_1 + n_2 + n_3 = \text{Total number of moles in the gas mixture.}\)

Dividing equation 2(a) by equation (4):

\[\frac{P_1 V}{PV} = \frac{n_1 RT}{\pi RT} \]

\[\frac{P_1}{P} = \frac{n_1}{\pi} \ldots (5)\]

Similarly from equation 2(b) and (4):

\[\frac{P_2}{P} = \frac{n_2}{\pi}, \quad \frac{P_3}{P} = \frac{n_3}{\pi}, \ldots \text{etc}\]

The fractions \(\frac{n_1}{\pi}, \frac{n_2}{\pi}, \ldots \text{etc.}\) are called the mole fractions of the respective gases.

The mole fraction of a constituent of any mixture is the number of moles of that constituent divided by the total number of moles in the mixture.

If \(\frac{n_1}{\pi}, \frac{n_2}{\pi}, \ldots = x_1, x_2 = \text{mole fraction}\), then equation (5) may be written:
\[ P_1 = X_1 P, \quad P_2 = X_2 P, \quad \text{etc.} \]

By this law, the partial pressure of any constituent of a mixture of ideal gases to be calculated from the total pressure at the same temperature, if the mole fraction is known.

The sum of mole fractions equal to 1

\[ X_1 + X_2 + X_3 + \ldots = 1 \]

Example

Mixture of gases consists of 0.495 gm gas \( A \) of molecular wt (M.wt = 66) and 0.182 gm gas \( B \) of (M.wt = 45.5). The total pressure is 76.2 cm of mercury. Calculate the partial pressure of the two gases.

<table>
<thead>
<tr>
<th>( \text{gm} )</th>
<th>( \text{M.wt} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.495</td>
</tr>
<tr>
<td>B</td>
<td>0.182</td>
</tr>
</tbody>
</table>

Total pressure \( P = 76.2 \)
Thermodynamics and Energy
The energy of a body is its capacity to do work (e.g., the kinetic energy of the body in motion, potential energy due to position, heat energy as measured by temperature, electrical energy, chemical energy).

The release of energy can be used to provide heat when a fuel burns in a furnace, or to produce electrical work when a chemical reaction pumps electrons through a circuit.

Thermodynamics - The study of the transformations of energy.

In physical chemistry, the universe is divided into two parts - the system and its surroundings. The system may be a reaction vessel, an engine, an electrochemical cell, a biological cell, etc. The surroundings are where we make our measurements.

The dynamic system is classified into 3 types:
1. Open system
   Matter can be transferred through the boundary between the system and its surroundings.
2. Closed system
   Matter cannot pass through the boundary.
3. Isolated system
   It is a closed system that neither mechanical nor thermal contact with its surroundings.

Open system
Exchange matter and energy with its surroundings

Closed system
Exchange energy with its surroundings, which may neither
but cannot exchange matter

Isolated system
A closed system
Mechanical nor thermal contact with its surroundings

Both open and closed systems can exchange energy with their surroundings (e.g.) a closed system can expand and
warming near the temperature at a light in the surroundings
and it may also transfer energy to them if they are at a lower temperature. An isolated system that has neither
mechanical nor thermal contact with its surroundings.

Energy density: \( \frac{\text{mass \times area \times length}}{\text{mass}} \) (e.g.)

\( \text{mass} = \text{kg} \)

Mechanical equivalent of heat
When a definite amount of any form of energy (e.g. mechanical, electrical) is converted into heat a perfectly
definite number of calories of heat is always produced.

1 calorie = 4.18 joules
Conservation of Energy

First Law of Thermodynamics

Although energy can be converted from one form to another, IT CANNOT BE CREATED OR DESTROYED.

Whenever a quantity of one kind of energy is produced an exactly equivalent amount of other kinds must disappear.

The law can also be stated in the following form:

The Total Energy of the System and its Surroundings Must Remain Constant although it May be Changed from one Form to Another.

Thermodynamic properties:

The energy of a system depends upon its pressure, volume, temperature, mass and composition. These four quantities are always related by an equation of state (P = f(V,T)). From Equation of state and mass and composition only two of the quantities if not P need be given, since the temperature is thereby determined.

Consider a system (gas, liquid or solid) represented by point A in Fig (1) if the conditions, volume (V) or pressure (P) are altered so that the system moves to B by path I and

Fig(1)-Energy change (Independent)

on path
as these brought back again to state (10) by
different path II.
Then, the total energy change in path I must be
identical with that in path II. (a direct consequence
of the first law of thermodynamics).
If the total energy change in path I is not identical
to that in path II, the motion or work would be
possible.
If the increase in energy involved in path I is greater
than the decrease in condensing path II, then by
condensing and the process \( A \to B \) by path I and
\( B \to A \) by path II, the system could be brought
back to its original state, but there would be a net
gain of energy. In other words, energy have been
created without the disappearance of an equivalent
amount of another kind. \( \times \) \( \delta \).
The resultant energy in passing from the state A
to the state B depends only on the initial and final
conditions, \( t \) and is independent of the path followed
in going from A \( \to \) B.

\[
\begin{align*}
\Delta E &= E_B - E_A \\
\text{Then, the change in energy in passing from } A \text{ to } B \text{ is} \\
\Delta E &= E_B - E_A \\
\text{(Here \( \Delta E \) is independent of the path).}
\end{align*}
\]
Let us assume that \( \Delta E_2 > \Delta E_1 \). This means that energy must have been created in going around the cycle by two different paths. This is in contradiction to the first law of thermodynamics, hence

\[
\Delta E_2 = - \Delta E_1
\]

\[
\Delta E_{\text{net}} = \Delta E_1 - \Delta E_2 = 0
\]
The properties of a system may be distinguished as being either Extensive or Intensive.

Extensive property: Depends upon the amount of the substance present in the system. If the quantity of material in the system is changed, the extensive property is changed in a proportional manner. Volume 'V' and mass 'm' are examples of extensive properties, heat capacity, internal energy, Entropy, etc.

Intensive property: A specific characteristic of the system and is independent of the amount of material concerned, e.g., Temp., density, surface tension, refractive index, viscosity, etc.

Potential All these properties are characteristics of the substance and are independent of the amount.

Work, Heat and Energy

Work (W) is done when an object is moved against an opposing force. Example of doing work is:

- The expansion of a gas which pushes out a piston and raises a weight.

A chemical reaction that drives an electric current through a resistance also does work because the same current could be driven through a motor and used to raise a weight.

When a system changes from one state to another, it may perform some kind of external work such as mechanical work of expansion, electrical work, etc.

The Energy of the system is its capacity to do work e.g., by compressing a gas or winding a spring. The capacity to do work is increased as the energy of the system is increased.
When the system does work (e.g., when the piston moves out or the spring uncoils), its energy is reduced because it can do less work than before.

The energy of the system (its capacity to do work) may be changed by means other than work itself; when the energy of a system changes as a result of a temperature difference between it and its surroundings, we say that the energy has been transferred as heat, e.g., when a heater is immersed in a beaker of water (the system), the capacity of the system to do work increases because hot water can be used to do more work than cold water.

Work is represented by the symbol \( W \).
- If \( W \) is positive if work is done by the system (e.g., expansion of a gas).
- If \( W \) is negative if work is done on the system (e.g., compression of a gas).

The system may absorb or evolve heat.

The quantity of heat is represented by \( Q \).
- \( Q \) is positive if the system absorbs heat.
- \( Q \) negative if heat is evolved by the system.

According to the First Law of Thermodynamics, the total system and surroundings must remain unaltered as the system changes from \( A \rightarrow B \) (Fig. 1).

Then the change in the internal energy \( \Delta E \)
\[ \Delta E = q - W \quad (\text{Mathematical statement of the 1st Law}) \]

The change in internal energy of the system \((\Delta E)\) must exactly equal to the energy absorbed in the form of heat \((q)\) from the surroundings minus the energy lost to the surroundings in the form of external work \((W)\):

\[ \Delta E_1 = E_B - E_A \]
\[ \Delta E_2 = E_A - E_B \]
\[ \Delta E_A \rightarrow A = \Delta E_1 + \Delta E_2 = 0 \]

\[ \Delta E_1 = -\Delta E_2 \]

For an infinitesimal process, the 1st Law is written as:

\[ dE = dq - dw \]

- \(dq\) = small change in the internal energy
- \(dq\) = amount of heat absorbed
- \(dw\) = external work done by the system

**Pressure-Volume work**

The work arising from a change in volume and pressure.

The work done by a gas as it expands and drives back the atmosphere, for example:

Chemical reactions resulting in the generation or consumption of gases (thermal decomposition of calcium carbonate or the combustion of carbon).

In order to find the pressure-volume work involved in the expansion of a gas against external force, consider a cylinder of cross-sectional area \(A\) fitted with a frictionless and weightless piston.

Let, Pressure on the piston \(P\).
Since pressure is force per unit area, the total force acting on the piston is:
\[ F = PA \]  \hspace{1cm} (1)

As a result of expansion, suppose the piston moves through a distance \(dl\).

The small amount of work done by the gas on the surroundings is:
\[ dW = F \, dl \]  \hspace{1cm} (2)

Substituting (1) into (2),
\[ dW = PA \, dl \]  \hspace{1cm} (3)

But \( dP \, dl = dV \) = increase in volume due to the movement of the piston.

Therefore,
\[ dW = PdV \]  \hspace{1cm} (4)

The total work in the expansion of the gas from initial volume \(V_i\) to the final volume \(V_f\) is then obtained by integrating equation (4) between the limits \(V_i\) and \(V_f\):
\[ W = \int_{V_i}^{V_f} PdV \]  \hspace{1cm} (5)

If this is the only type of work done by the system, then substitution of equation (5) in the first law expression gives:
\[ \Delta E = q - \int PdV \]  \hspace{1cm} (6)
Equations (5) and (6) are perfectly general and can be utilized to calculate $W$, $q$, and $\Delta E$ in any expansion and compression of the system.

Special cases

(a) Constant volume
When there is no change in volume, $\Delta V = 0$ and equation (6) takes the form:

$$\Delta E = q$$

(i.e.) Any thermal change occurring in the calorimeter at constant volume must be the change in the internal energy due to the chemical reaction or physical transformation.

(b) Opposing pressure Zero
When the gas expands against a zero external pressure, no work is done and hence again:

$$\Delta E = q$$

This type of expansion is called free expansion.

(c) Opposing pressure constant
When $P$ is constant, equation (5) becomes:

$$W = P (V_2 - V_1)$$

and equation (6) becomes:

$$\Delta E = q - P (V_2 - V_1)$$

(d) Opposing pressure variable
When $P$ is variable, it must be known as a function of volume. So equation (5) can be integrated and
or the integration is carried out graphically by plotting $P$ versus $V$ and determining the area under the curve. When $W$ is known, it can be substituted into equation (6) to determine $AE$ or $Q$.

In all calculations of $W$ involving gas expansion it must be kept in mind that when a volume change occurs the amount of work done by the gas on the surroundings depends on the pressure that the surroundings exert on the system rather than the pressure within the system itself.

Note that the pressure in equation (6) is always one quantity. $W$ will be positive if $V_f > V_i$ (expansion).

A positive value of $W$ means that work is done by the gas on the surroundings. This is what happens when a system expands pushing back its surroundings.

On the other hand if $V_f < V_i$, then we have a Compression.

$W$ is negative and work is done by the surroundings on the gas.

**Conclusion**

In any expansion, the system does work.

In a compression, work is done on the system.

**Reversible Processes**

Reversible processes are processes that may be reversed at any moment by changing an independent variable by an infinitesimal amount. A process is said to be reversible when the properties of the system at every instant remain uniform during the process. It can be described as a succession of states each of which is in a state of equilibrium.

Reversible process is an extremely slow process and would
If the gas is compressed, the final volume is smaller $(V_e < V_i)$ and $W_{rev}$ is positive $(W > 0)$. That means the work is done on the gas $(w_g)$.

Example: How much work we get from the expansion of 1 mole of a perfect gas by a factor of $(10)$ at $273 \degree C$ ?

Solution: $W_{rev} = -RT \ln \frac{V_e}{V_i} = -6229 \text{ J mol}^{-1}$

When $V_e < V_i$ — compression — $W > 0$ work is done on the gas

When $V_e > V_i$ — expansion — $W < 0$ work is done by the gas

Example

Calculate the maximum work in ergs for the expansion of 1 mole of an ideal gas from a volume of 10 liters to 20 liters exactly at 25$^\circ$C.

Since for a perfect gas at constant temperature

$$ \frac{P_i V_i}{T} = \frac{P_e V_e}{T} \text{ (at constant temp.)} $$

so that

$$ \frac{V_e}{V_i} = \frac{P_i}{P_e} $$

Substituting in equation (8), the maximum work in isothermal expansion can also be written as:

$$ W_{rev} = -RT \ln \frac{P_i}{P_e} \quad \text{--- (9)} $$
\[ \begin{align*}
\text{Calculate: } & \quad \text{for } \theta = \frac{1}{300} \text{ rad sec}^{-1} \\
& \quad \text{at } a = 1.0 \text{ in } \text{engr. units} \\
\end{align*} \]
require an infinite time.

In irreversible processes, the change is produced rapidly and the system does not have time to achieve equilibrium. Reversible processes are of great importance because they yield the maximum amount of work obtained from a given net change. In irreversible processes, less work is obtained than would be required to return the system to its initial state. (e.g.)

Reversible expansion \( W_{rev} = -\int \frac{P \, dV}{V} = \text{Total work of expansion} \) - (7)

**Conclusion:** Only if the expansion is carried out reversibly at constant temperature can sufficient energy be obtained to reverse the process compressing the gas to its original conditions.

**Reversible Isothermal Expansion of a Real Gas**

The system in thermal contact with its surroundings

\[ P V = nRT \]  
(Equation of state)

The pressure at each stage of expansion is expressed as

\[ P = \frac{nRT}{V} \]

where \( P, V \) are pressure and volume at each stage of expansion.

\( n, R \) are constants.

Substituting \( P \) in equation (7) we obtain:

\[ W_{rev} = -nRT \int \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i} \] - (8)
Heat Capacity

The heat capacity of a system is defined as the heat required to raise the temperature of the system by one degree.

\[ C = \frac{dq}{dT} \]  \hspace{1cm} (1)

\( dq \) is the heat absorbed when the temperature is raised by \( (1) \) degree

The heat capacity at constant volume and pressure is given by:

\[ C_v = \frac{dE_v}{dT} \]  \hspace{1cm} (at const. volume) \hspace{1cm} (2)

\[ C_p = \frac{dE_p}{dT} \]  \hspace{1cm} (at const. pressure) \hspace{1cm} (3)

The internal energy \( (E) \) of a substance increases when the temp. is raised. This increase depends on the conditions under which the heating takes place.

The heat absorbed at constant volume is equal to the increase in internal energy under the same conditions.

\[ dE_v = dq \]

Equation (2) may be written as

\[ C_v = \frac{dE_v}{dT} \]  \hspace{1cm} (const. volume) \hspace{1cm} (4)

The internal energy is a function of \( F \) and \( V \). For an ideal gas, \( E \) is independent of the volume. Therefore:

\[ C_v (\text{ideal gas}) = \frac{dE}{dT} \]

The heat capacity is **extensive property** (e.g., 100 g of water has 100 times the heat capacity of 1 gm of steel and therefore requires 100 times the heat to bring about...
Some rise in temperature

Molar heat capacity at constant volume, \( C_v \), is the heat capacity per mole of material and is an intensive property. All molar quantities are intensive.

Specific heat capacity of a substance is the heat capacity of a sample divided by the mass, usually in grams (e.g., the specific heat capacity of water at room temp (25°C) is close to \( 4.18 \times 10^3 \) J/kg°C).

The heat capacity can be used to relate a change in the internal energy (\( U \)) to a change in temperature (\( T \)) at constant volume system.

\[
dE = C_v \, dT \quad \text{at constant volume}
\]

This is the infinitesimal change in temp change about an infinitesimal change in internal energy and the constant proportionality is the heat capacity at constant volume (\( C_v \)).

\[
\Delta E = C_v \Delta T \quad \text{(at const. volume)}
\]

\[
\frac{dE}{dT} = C_v
\]

This relation provides a simple way of measuring the heat capacity of a sample, e.g.,

A measured quantity of heat is supplied to the sample (e.g., electrically) and the resulting increase in temperature is monitored. The ratio of the heat supplied to the temperature rise is the heat capacity of the sample.

A large heat capacity means that for a given quantity of heat, there will be only a small increase in temperature, the sample has a large capacity for heat, and
An infinite heat capacity means that there will be no increase in temperature however much heat is supplied. At a phase transition (such as boiling point), the temperature of water does not rise as heat is supplied and means the energy is use to drive endothermic phase transition (to vaporize the water) rather than to increase its temperature. So at the temperature of the phase transition, the heat capacity of a sample is infinite (co).

Example 1: Most systems expand when heated at constant pressure. Such systems do work on the surroundings and some of the energy supplied to them as heat escaped back to the surroundings. As a result, the temperature of the system rises less than when the heating occurs at constant volume. A smaller increase in temperature means a larger heat capacity, \[ C = \frac{dE}{dT} \]

At constant pressure, the heat capacity of a system is larger than the heat capacity at constant volume.

For a perfect gas \((PV = nRT)\)

At constant press. \[ P\left(\frac{dV}{dT}\right)_P = nR \]

The relation between the heat capacities of a perfect gas

\[ C_p - C_v = nR \]

The heat capacities of a perfect gas at constant press. and constant volume differ from each other by a constant amount equal to the gas constant \((R)\).
Enthalpy

The change in internal energy is not equal to the heat supplied when the system is free to change its volume. Under these circumstances some of the energy supplied as heat to the system is returned to the surroundings as expansion work, so \( dE \) is less than \( dq \) \( (dE = dq - W) \). In this case, the heat supplied at constant pressure is equal to the change in another thermodynamic property of the system, called the "Enthalpy". As constant-pressure processes are more common in chemistry than constant-volume processes because most operations are carried out in open vessels, and if only pressure-volume work is done and the pressure is constant, the work done on the system will be:

\[
W = \int P \, dV
\]

\[
E = q - W
\]

\[
E_2 - E_1 = q - P (V_2 - V_1)
\]

\( V_i \) = Initial volume \( E_i = \) Initial internal energy

\( V_f \) = Final \( E_f = \) Final

So that the heat absorbed in equation (3) is given by:

\[
q = E_2 - E_1 + PV_2 - PV_1
\]

\[
q = (E_2 + PV_2) - (E_1 + PV_1)
\]

The heat absorbed is equal to the difference of two quantities that are functions of the state of the system

\[ H = E + PV = \text{Enthalpy} \]

\( E, P, V \) are state functions. Then the enthalpy \( H \) is a state func
The change in enthalpy (ΔH) between any pair of initial and final states is independent of the path between them.

\[ H_2 - H_1 = ΔH = q_p \]

At constant pressure, the change in enthalpy is equal to the heat supplied to the system (if the only work done is the pressure-volume work).

**Example:** To calculate ΔE and ΔH in a constant volume calorimeter, the evolution of heat (q) is the measure of the decrease in internal energy (ΔE)

\[ q = ΔE \]

In a constant pressure calorimeter, the evolution of heat (q) is a measure of the decrease in enthalpy (ΔH)

\[ q = ΔH \]

**Proof:** [DIAGRAM]

When pressure-volume work is the only kind of work

\[ H = E + PV \]  \hspace{1cm} (1) \]

For a general infinitesimal change in the state of the system, E changes to \( E + dE \), \( P \) changes to \( P + dP \) and \( V \) changes to \( V + dV \), so \( H \) changes from \( (E + PV) \) to:

\[ H + dH = (E + dE) + (P + dP) \times (V + dV) \]

\[ H + dH = E + dE + PV + PdV + VdP + dPV \]

The term \( dPV \) is the product of two infinitesimal small quantities and can be neglected, and we have:

\[ H = E + PV \]

Thus equation (2) becomes:

\[ H + dH = H + dE + PdV + VdP \]

\[ dH = dE + PdV + VdP \]

we know that:

\[ dE = dq + dW \]

Substituting equation (5) into equation (4), we get
\[ \text{d}H = \text{d}q + \text{d}w + P \text{d}V + V \text{d}P \quad - - - (6) \]

If the system is in mechanical equilibrium with its surroundings at a pressure \( P \) and does only expansion work, then:
\[ \text{d}w = -P \text{d}V \quad - - - (7) \]

Substitute (7) into (6) we get:
\[ \text{d}H = \text{d}q - P \text{d}V + P \text{d}V + V \text{d}P \]
\[ \text{d}H = \text{d}q + V \text{d}P \quad - - - (8) \]

When the heating occurs at constant pressure then:
\[ dP = 0 \quad (\text{no change in pressure}) \]

\[ \{ \frac{\text{d}H}{dP} = \frac{\text{d}q}{dP} \} \quad \text{at constant pressure} \]

[At constant pressure, the change in entropy is equal to the heat supplied to the system.]

Adiabatic Processes

An adiabatic process is one in which there is no change of heat between the system and its surroundings (i.e., the system is thermally isolated from its environment.)

Since no heat enters or leaves the system, then \( (q = 0) \)

and work is done at the expense of the internal energy of the gas and the temperature drops.

Since if work is done on the system, the internal energy of the system \( (E) \) will increase. Conversely if work is done by the system, the internal energy of the system decreases and consequently the temperature of the system drops.

From the first law, we have \( \text{d}E = q - w \)

For adiabatic process, \( q = 0 \)

\[ \text{d}E = -w = -P \text{d}V \quad - - - (9) \]

since \( \text{d}E = C \text{d}T \quad - - - (10) \)
Isothermal process

In isothermal process the temperature is maintained constant during the entire operation and \( pv = \text{constant} \). For the same initial pressure and volume \((p_i, V_i)\), isothermal expansion results in a larger final pressure than the final pressure for adiabatic expansion \((p_{\text{adiabatic}} < p_{\text{adiabatic}})\). The reason for this lies in the fact that adiabatic expansion is accompanied by a fall in temperature which will diminish the volume, but in isothermal process the temperature is constant.

When a gas expands adiabatically to a larger volume and lower pressure, the volume is smaller than it would be after an isothermal expansion to the same pressure.

The work done by the isothermal reversible expansion of the gas represented by the area under AB is larger than the work done by the reversible adiabatic expansion represented by the area under AC. The energy for doing the additional work in the isothermal expansion is provided by the heat absorbed from the constant temperature reservoir. The energy for doing work in the adiabatic expansion comes from the cooling of the gas itself.

![Diagram showing isothermal and adiabatic expansions]
\[ C_v = C_p = nR \]

The heat capacities of a perfect gas at constant pressure and constant volume differ from each other by a constant (R).

The relationship between the heat capacities at constant pressure and constant volume for a perfect gas is

\[ \frac{C_v}{C_p} = \frac{1}{n} \]

At constant pressure, the heat capacity of a system is

\[ \frac{\Delta U}{\Delta T} = \frac{\Delta E}{\Delta T} \]

A smaller increase in temperature means a larger heat supplied to the system at constant volume.

Example: Water expands when heated, as the temperature increases. The heat capacity of water is finite. At a phase transition (such as boiling), the water is supplied heat and the temperature of the water increases. This means that the energy is used to drive the water from the liquid phase to the gas phase.

An infinite heat capacity means that there will be no increase in temperature, however much heat is supplied.
**Enthalpy**

The change in internal energy is not equal to the heat supplied when the system is free to change its volume. Under these circumstances some of the energy supplied as heat to the system is returned to the surroundings as expansion work. So \( dE \) is less than \( dq \) \( (dE = dq - W) \). In this case, the heat supplied at constant pressure is equal to the change in another thermodynamic property of the system called the "Enthalpy".

As constant-pressure processes are more common in chemistry than constant-volume processes because most operations are carried out in open vessels, and if only pressure-volume work is done and the pressure is constant, the work done on the system will be:

\[
W = -P\Delta V \quad \quad (1)
\]

\[
\Delta E = q - W
\]

\[
E_2 - E_1 = q - P(V_2 - V_1) \quad \quad (2)
\]

\( E_2 \) = Final internal energy \( E_1 \) = Initial internal energy

\( V_1 \) = Initial volume \( V_2 \) = Final volume

So that the heat absorbed in equation (3) is given by:

\[
q = E_2 - E_1 + PV_2 - PV_1 \quad \quad (4)
\]

\[
q = (E_2 + PV_2) - (E_1 + PV_1)
\]

The heat absorbed is equal to the difference of two quantities that are functions of the state of the system.

Set \( H = E + PV \) = Enthalpy.

\( E, P, V \) are state functions; then the enthalpy \( H \) is a state function.
The change in enthalpy ($\Delta H$) between any pair of initial and final states is independent of the path between them.

$$H_1 - H_0 = \Delta H = q_p$$

At constant pressure, the change in enthalpy is equal to the heat supplied to the system (if the only work done is the pressure-volume work).

Example: To calculate $\Delta E$ and $\Delta H$ in a constant volume calorimeter, the evolution of heat ($q$) is the measure of the decrease in internal energy $\Delta E$ ($q = \Delta E$).

In a constant pressure calorimeter, the evolution of heat ($q$) is a measure of the decrease in enthalpy ($\Delta H$) ($q = \Delta H$).

Proof:

When pressure-volume work is the only kind of work:

$$H = E + PV$$

For a general infinitesimal change in the state of the system, $E$ changes to $E + dE$, $P$ changes to $P + dP$, and $V$ changes to $V + dV$, so $H$ changes from $(E + PV)$ to:

$$H + dH = (E + dE) + (P + dP) \times (V + dV)$$

$$H + dH = E + dE + PV + PdV + VdP + dPdV$$

The term $(dPdV)$ is the product of two infinitesimal small quantities and can be neglected and we:

$$H = E + PV$$

Then equation (1) becomes:

$$H + dH = E + dE + dPdV + VdP$$

$$dH = dE + PdV + VdP$$

we know that:

$$dE = dq + dW$$

Substituting equation (5) into equation (4), we get:
\[ dH = dq + dw + PdV + VdP \]  \hspace{1cm} (6)

If the system is in mechanical equilibrium with its surroundings, then pressure \( P \) and does only expansion work, then:

\[ dw = - PdV \]  \hspace{1cm} (7)

Substitute (7) into (6) we get:

\[ dH = dq - PdV + PdV + VdP \]

\[ dH = dq + VdP \]  \hspace{1cm} (8)

When the heating occurs at constant pressure then:

\[ dq = 0 \]  \hspace{1cm} (no change in pressure)

\[ dH = dq \]  \hspace{1cm} (at constant pressure)

[At constant pressure, the change in enthalpy is equal to the heat supplied to the system.]

**Adiabatic Processes**

An adiabatic process is one in which there is no exchange of heat between the system and its surroundings (i.e., the system is thermally isolated from its environment).

Since no heat enters or leaves the system, then \( (dq = 0) \) and work is done at the expense of the internal energy of the gas and the temperature drops.

\[ \text{If work is done on the system, the internal energy of the system (U) will increase. Conversely, if work is done by the system, the internal energy of the system decreases and consequently the temperature of the system drops.} \]

From the First Law, we have:

\[ \Delta E = q - w \]

For adiabatic process, \( q = 0 \)

\[ \Delta E = -w = -PdV \]  \hspace{1cm} (9)

Since:

\[ \Delta E = C dT \]  \hspace{1cm} (2)
Ex. Determine the work of isothermal reversible expansion of 3 moles of water vapor from 0.5 x 10^5 to 0.2 x 10^5 Pa at 330 K.

Water vapor obeys the law of ideal gases, so:

\[
W = nRT \ln \frac{V_2}{V_1}
\]

\[
= nRT \ln \frac{V_2^2}{V_1^2}
\]

\[
W = 3 \times 8.314 \times 330 \times \ln \frac{0.5 \times 10^5}{0.2 \times 10^5}
\]

\[
= 7.541 \times 10^3 \text{ J}
\]

Ex. How much work is done in the adiabatic expansion for the expansion of a perfect gas from 28.4 L to a volume of 44.9 L.

\[
W = \int C_v \, dT = \frac{R \, \ln \frac{V_1}{V_2}}{\gamma - 1}
\]

\[
W = 3 \times 8.314 \times \ln \frac{28.4}{44.9}
\]
Substituting eq. (2) into (1)

\[ C \, dT = -P \, dV \quad \cdots (3) \]

For an ideal gas, \( PV = nRT \)

For 1 mol, \( P = \frac{RT}{V} \)

Substituting the value of \( P \) into eq. (3)

\[ C \, dT = -\frac{R \, T}{V} \, dV \]

\[ C \, \frac{dT}{T} = -\frac{R \, dV}{V} \quad \cdots (4) \]

assuming that \( C \) is independent on temp.

\[ C_v \int_{T_1}^{T_2} \frac{dT}{T} = -R \int_{V_1}^{V_2} \frac{dV}{V} \]

\[ C_v \ln \frac{T_2}{T_1} = R \ln \frac{V_1}{V_2} \quad \cdots (5) \]

Equation (5) is an approximate equation for reversible adiabatic expansion.

In adiabatic expansion, if \( T_2 < T_1 \), Temp will fall

Compression \( T_2 > T_1 \), \( \Delta T \) is rise

Reversible work in adiabatic expansion

\[ \Delta E = W - q \]

For adiabatic expansion, \( q = 0 \)

\[ \Delta E = W \]

\[ \Delta E = C_v \Delta T \]

\[ \sqrt{\Delta E} = W = \int C_v \, dT = C_v \ln \frac{T_2}{T_1} - R \ln \frac{V_1}{V_2} \]
Joule-Thomson effect

A gas from a high pressure region (A) is allowed to pass to a low pressure region (C) through a throttle (B) which consists of a porous plug.

The gas emerging at (C) attains an equilibrium and its temperature can be measured directly. The entire system is thermally isolated so that the process is an adiabatic one (q=0).

Let $P_1, V_1, T_1$ be the pressure, volume and temperature of the gas before it expands and $P_2, V_2, T_2$ be the final pressure, volume and the temperature of the gas.

The work done on the gas before it is forced through the porous plug will be $W = P_1 V_1$, and the work done by the gas in expansion will be $W = P_2 V_2$ and hence the net work done by the system:

$$W = P_2 V_2 - P_1 V_1$$

Since the process is being carried out adiabatically, then $q=0$ and therefore applying the first law:

$$\Delta E = E_2 - E_1 = W = -(P_2 V_2 - P_1 V_1)$$

$$E_2 - E_1 = P_1 V_1 - P_2 V_2$$

$$E_2 + P_2 V_2 = E_1 + P_1 V_1$$

Since, $H = E + PV$

$$H_2 = H_1 \quad \text{or}$$

$$\Delta H = 0 \quad \text{for adiabatic process (proof)}$$

(The heat content of a system during its expansion remains constant)
Isothermal Process

In isothermal process the temperature is maintained constant during the entire operation and $PV = \text{constant}$.

For the same initial pressure and volume ($P_i, V_i$), isothermal expansion results in a larger final pressure than the final pressure for adiabatic expansion ($P_i, \text{adiabatic} > P_i, \text{isothermal}$).

The reason for this lies in the fact that adiabatic expansion is accompanied by a fall in temperature which will diminish the volume, but in isothermal process the temperature is constant.

When a gas expands adiabatically, its a larger volume and lower pressure, the volume is smaller than it would be after an isothermal expansion to the same pressure.

The work done by the isothermal reversible expansion of the gas represented by the area under $AB$ is larger than the work done by the reversible adiabatic expansion represented by the area under $AC$. The energy for doing the additional work in the isothermal expansion is provided by the heat absorbed from the constant temperature reservoir. The energy for doing work in the adiabatic expansion comes from the cooling of the gas itself.
Thermochemistry

Term is the subject that deals with the study of how energy changes in a chemical reaction, expressed in terms of heat. The laws of thermodynamics are fundamental principles used in thermochemistry. Energy is either released or absorbed during a chemical reaction. The energy change in a reaction is represented by a change in the total enthalpy of the system.

Heat is a form of energy transfer that occurs between two systems at different temperatures. The direction of heat transfer is from the system with a higher temperature to the system with a lower temperature. Heat transfer can occur through conduction, convection, or radiation.

The first law of thermodynamics states that energy cannot be created or destroyed, only converted from one form to another. This law is also known as the law of conservation of energy. The second law of thermodynamics states that heat always flows from a system with a higher temperature to a system with a lower temperature.

During a chemical reaction, the product is formed from the reactants. The yield of the reaction can be quantified by the percentage yield, which is the ratio of the actual yield of the product to the theoretical yield.
Standard state for the heat of reaction

The value of enthalpy (H) and entropy (S) will depend on the temperature and pressure of the surroundings. The temperature of 25°C (298 K) and pressure of 1 atm are generally used as standard conditions for substances (pure solids, liquids, and ideal gases).

If the reactants and products are in the standard state (25°C and 1 atm), the heat transferred is called the standard heat for that reaction referred as ΔH°, ΔH° standards i.e., the initial and final substances are in their standard states. More recently, the standard state is defined at pressure of 1 atm. at any specified temperature. The standard state at a specific temperature is its pure form at 1 atm. example: the standard state of pure ethanol (C₂H₅OH) at 25°C (298 K).

Pure liquid ethanol at 25°C is a standard state. The standard state condition in terms of pure solid iron.

The standard change in enthalpy (ΔH°) is a measure of how much energy is released or absorbed.
Process is the difference between the molar heat of formation in their standard states and enthalpy of the reactants in their standard states.

Example: for a standard enthalpy change in 1 mole of the standard enthalpy of formation (enthalpy change per mole). The phase change of water at 1 bar. Water condenses from vaporizes to gas at 1 bar.

$$\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g) \quad \Delta H^\circ_{\text{vap}}(298\text{ K}) = +80\text{ KJ/mol}$$

The standard enthalpy ($\Delta H^\circ$) may be reported for any temperature. However, the conventional temp. for reporting Thermodynamic data is (298 K). All thermodynamic data will refer to this conventional temp. unless otherwise mentioned.

Examples: The reaction between solid carbon (graphite) and gaseous oxygen to yield carbon dioxide gas at 298 K.

\[ \text{C(graphite)} + \text{O}_2(g) \rightarrow \text{CO}_2(g) \quad \Delta H^\circ_{298} = -393.5\text{ Kcal} \]

This means that when 1 mole (12 gms) of solid carbon and 1 mole (32 gms) of gaseous oxygen react completely at 298 K, to yield 1 mole (44 gms) of gaseous carbon dioxide at constant pressure (labor), there is a decrease in enthalpy, since $\Delta H$ is negative of 393.5 Kcal. The negative value of $\Delta H$ means that the enthalpy of the products is less than that of the reactants at the specified temp. In other words, the reaction at a given temp. is associated with an evolution of heat.

$\Delta H$ is negative, the reaction is exothermic.

The standard heats of formation of chemical compounds are tabulated in index tables.
Due to formation

The chemical reactions of elements in nature are
formed from its elements in their standard states to their
stable forms at ordinary temperature and pressure.
In the reaction between carbon (C) and oxygen to form
Carbon dioxide (CO₂), the standard heat of reaction is:
$\Delta H_{f}(\text{CO}_2) = -393.5 \text{ kJ/mol}$

This is the stable form of carbon and hence it is in its standard
state of the element.

Example

The thermodynamic expression for the formation of
hydrogen iodide is:

$$\text{H}_2 + \text{I}_2 \rightarrow 2 \text{HI} \quad \Delta H_f(\text{HI}) = -86.1 \text{ kJ/mol}$$

The composition of simplicity in calculation, the heat of reaction
$\Delta H_f$ can be calculated by assuming the standard State to be
their standard states to be zero and noting the change
in the heat of formation.

The formation of hydrogen iodide from its elements:

$$\text{H}_2(g) + \text{I}_2(g) \rightarrow 2 \text{HI(g)} \quad \Delta H_f = -86.1 \text{ kJ/mol}$$

Note: $\Delta H_f$ is formed from the elements. There is
a decrease in energy in enthalpy as the reaction proceeds.
$\Delta H_f$ is negative for exothermic $\Delta H_f$ and positive for
endothermic.
Example 1

Consider the reaction:

\[ AB + 2CD \rightarrow D_2 + 2BC \]

Example 2

By the law of conservation of mass, all substances present before the reaction must be present after the reaction. The only substance remaining before and after the reaction is water (H_2O), indicating the water is a product of the reaction.

Heat of combustion

It is the enthalpy change of the complete combustion of one mole of a compound.

Heat of combustion of benzene (C_6H_6): -381.8 kcal/mol

The heat of combustion of a compound is negative since the process is exothermic.
Thermochemical Laws

The laws of thermochemistry are based on the principle of conservation of energy, and hence on the first law of thermodynamics.

The first law of thermodynamics was given by van der Waals and Laplace in 1789, stated that:

The quantity of heat which must be supplied to decompose a compound into its elements is equal to the heat evolved when the compound is formed from its elements.

Thus, if the reverse of a chemical reaction is written, the sign of ($\Delta H$) is changed, but its magnitude remains same:

$$\Delta H (A \rightarrow B) = -\Delta H (B \rightarrow A)$$

Example - the heat evolved when water is formed from hydrogen and oxygen is exactly equal to the heat absorbed when water decomposes into hydrogen and oxygen.
The second law of thermodynamics discovered by Hess in 1840. The overall heat change in a chemical reaction carried out either at constant pressure or at constant volume is the same irrespective of the fact whether the reaction proceed in one or several steps. (The Law of constant heat summation)

This is a direct consequence of the first law of thermodynamics according to which $\Delta E$ and $\Delta H$ are equal to the heats of reaction at constant volume and constant pressure respectively and are dependent only on the initial and final states of system. (Constant volume, $q = \Delta E$); (Constant pressure, $q = \Delta H$)

**Example:** (the law of constant heat summation).

\[ \text{Energy change at constant pressure} + \text{Energy change at constant volume} = \text{Overall Energy change} \]

**Note:** Be sure to use the correct units and check your work.
\[
\text{Vapor} + \text{H}_{2} \rightarrow \text{H}_{2} + \text{H}^{+} (\text{aq}) \quad \Delta G \text{ or } E(\text{aq})
\]

In some cases, heat energy - \text{Enthalpy}

The reaction is then converted and shows advancement in aspect as:

\[
\text{NH}_{3}(\text{aq}) (2 \text{M}) \rightarrow \text{NH}_{4}^{+} (\text{aq}) + \text{H}^{+} (\text{aq})
\]

\[
\text{HCl}_{(\text{aq})} (2 \text{M}) \rightarrow \text{H}^{+} (\text{aq}) + \text{Cl}^{-} (\text{aq})
\]

The results had indicated a shift in the reaction. This can be explained by the second. Bases are subject to acid in a way that:

\[
\text{NH}_{3}(\text{aq}) (2 \text{M}) + \text{HCl}_{(\text{aq})} (2 \text{M}) \rightarrow \text{NH}_{4}^{+} (\text{aq}) + \text{H}^{+} (\text{aq})
\]

The reaction seems like an acid-base reaction. The acid-base interaction is a strong one. The bond change in some aspects of them.

The importance of acids and bases to be able to work and change reactants or products. It is possible that the concentration of one molecule can influence the concentration of another molecule. Therefore, these reactions can be used to determine

\[
\text{NH}_{3}(\text{aq}) + \text{H}_{2} \rightarrow \text{NH}_{4}^{+} (\text{aq}) + \text{H}^{+} (\text{aq})
\]

The concentration of acids and bases can be used to do the work but are also used for other interactions. It is possible to have a combination of both. This is why it is important to understand the mechanisms behind these reactions.
Heat of Solution

The measure of heat evolved or absorbed by the solution of a solute in a solvent is a property termed 'heat of

\[
\text{Heat of Solution} = \text{Heat evolved or absorbed}
\]

When a substance is dissolved in a liquid solvent, a change in the strength of concentration of the acid at infinite dilution.

\[
\text{HCl}_{(aq)} = \text{HCl}_{(aq)} \text{ (aqueous solution)}
\]

The heat evolved in the dilution of solutions from one concentration to another concentration is called the enthalpy of dilution.

Hence, the heat evolved when 1 mole HCl (50 ml) is neutralized by a base is equal to:

\[
\text{Heat evolved} = \text{Heat of neutralization} = 1540 \text{ cal} = 6410 \text{ J}
\]

Heat of Neutralization

When aqueous solutions of acids and bases react, heat is evolved.

The heat of neutralization of the acid is the change in enthalpy when one gram equivalent of acid is neutralized by one gram equivalent of a base in solution.
The trend of neutralization of strong acids and strong bases is practically the same as in the Andy reaction.

HCl + NaOH → NaCl + H₂O

This neutralization of HCl by NaOH can be represented as:

\[ \text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} \]

Hence, every neutralization of a reaction involves the same reaction of H⁺ and OH⁻ ions to form neutralized water.

The trend of neutralization of a reaction of a weak acid and a weak base is not reversed because the reaction does not occur. The neutralization of a strong acid with a strong base also holds true.

**Example**: The neutralization of acetic acid by sodium hydroxide solution

\[ \text{CH}_3\text{COOH} + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O} \]
Exercise

The rate of neutralization of hydrocyanic acid.

\[ \text{Rate} = -29 \text{ kcal/gm-equiv} \]

Calculate the heat of neutralization at 20°C.

\[ \text{Heat} = -29 \times \text{mol} \times 20 \text{C} \]

Variation of heat of reaction with temperature

The enthalpy of the general reaction:

\[ \Delta H = \text{Enthalpy of reactants} - \text{Enthalpy of products} \]

Coefficient of thermal expansion of the substance with respect to temperature can get:

\[ \left( \frac{dH}{dT} \right)_P = C_p \times \Delta T \]

The change in heat capacity at constant pressure is:

\[ C_p = \left( \frac{dH}{dT} \right)_P \]

Therefore:

\[ \left( \frac{dH}{dT} \right)_P = C_p \times \Delta T \]

\[ \text{or} \quad \left( \frac{dH}{dT} \right)_P = \Delta C_p \]
Exercise

The standard heat of formation of liquid water is 68.3 kcal at 25°C. Calculate the value at 35°C.

The molar heat capacities at constant pressure in the given temperature range are:

\[ \Delta C_p, H_2O = 68.9 \text{ cal/deg mole} \]
\[ \Delta C_p, O_2(g) = 69.7 \text{ cal/deg mole} \]

Solution

\[ \Delta H_f = -68.3 \text{ kcal} \]

\[ H_f = H_f^0 + \Delta H_f \text{ kcal/mol} \]

\[ \Delta H_f = -68.3 \text{ kcal/mol} \]

\[ T = 298 \text{ K} \]

\[ \Delta H_f = \Delta H_f \left( \frac{T_f}{T} \right) \]

\[ \Delta H_f = -68.3 \times \left( \frac{358}{298} \right) \]

\[ \Delta H_f = -66.2 \text{ kcal/mol} \]
Calorimetric Measurements

The calorimeter is used to measure the heat change in a chemical reaction by changing the molar heat capacity (enthalpy change) in a solution. Let's assume a definite amount of water, B, is added to the calorimeter, an aqueous solution. The heat, Q,

The heat change of the reaction equals the product of the molar heat of the water and the heat capacity of the water and the reaction.

\[ q = \Delta H \]

Bond Enegy:

The bond energy is defined as the average amount of energy (per mole) required to break a particular bond in a molecule, producing free atoms or radicals. Thus, the C-H bond energy is the amount required to dissociate 1 mole of methane (CH₄) into gaseous carbon and hydrogen atoms:

\[ (CH₄) \rightarrow C + 4H \]

The chemical reaction, like H₂ + O₂, as well as any other reaction, require this energy to break chemical bonds. In a chemical reaction, the energy required to break a bond is often smaller than that required to form a bond. For example, the energy required to break C-H bond is about 414 kJ/mol, whereas the energy needed to form a C-H bond is about 414 kJ/mol. Therefore, the bond energy in a polyatomic compound is the average amount of energy required to break the bond.
\[ \Delta H_f^{\circ} = 1 \times 10^{-3} \times \left( 2 \times 10^3 - \left( -1 \times 10^3 \right) \right) = -205 \times \text{kJ} \]

Heat of combustion.

The enthalpy change accompanying the complete combustion of 1 mole of a compound.

Organic compounds can be burnt in oxygen to give carbon dioxide and water as the sole products. \( \text{C}_x\text{H}_y\text{O}_z \rightarrow x\text{CO}_2 + \frac{y}{2}\text{H}_2\text{O} \) and the standard heat of formation, \( \Delta H_f^{\circ} \), of the substances are in their standard states.

The value for a number of familiar compounds can be found in index tables. The combustion products are assumed to be \( \text{CO}_2 \) and liquid \( \text{H}_2\text{O} \) in each case.
The figure represents a student's handwritten notes on a chemistry problem. The notes contain mathematical equations and chemical reactions. The handwriting is clear, and the notes are well-organized on the page. The student has written equations and calculations related to chemical reactions and thermodynamics. The page includes the following calculations and equations:

\[ \text{For liquid ethanol:} \quad \Delta H^\circ = -66.36 \text{ kcal} \]

\[ 2\text{C}_2\text{H}_5\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 5\text{H}_2\text{O} \quad \Delta H^\circ = -36 \text{ kcal} \]
Calorimetry Measurements

The calorimetry method of measuring the heat change involved in chemical reactions by changing the temperature of a known mass of water by an amount, is related to the amount of heat absorbed or released in the reaction. The change in temperature of the water can be measured.

\[ \Delta H = m \cdot \Delta T \]

Bond Energies

The bond energy is defined as: The average amount of energy (per mole) required to break a particular bond in a molecule, producing free atoms or radicals. Thus, the C-H bond energy is the amount required to dissociate 1 mole of methane (CH₄) into gaseous carbon and hydrogen atoms:

\[ \text{CH}_4 \rightarrow \text{C} + 4\text{H} \]

The chemical reaction takes the form in which a molecule and the heat energy released when the bonds are broken. The energy required to break a bond is related to the bond's strength and can be compared for different examples. For example, the energy required to break a bond in alcohol (C₂H₅OH) or water is different, so the energy required for each bond is different. Therefore, the bond energy is dependent on the molecules involved in the reaction, the amount of energy required to break bonds.
a particular bond at one of the compounds' graphs. The bond may be considered as:

\[ \hat{r} = \hat{r} + \hat{r}' \]

Addition of a bond and its inverse is the main idea. Indeed, this combination of bonds in the bond energy will be the energy of the system. The different methods such as the bond-breaking and bonding determine energy per devoted.

\[ \Delta E \text{ (bond)} = \frac{\alpha}{2} \text{ new} \]

The bond energy is then obtained from the equation, and all the bonds are divided. \( \alpha = 2n \) or \( \alpha = \frac{1}{4} \)

Example: The bond of sodium \( \hat{r} = \frac{2}{3} \) and \( \hat{r} = \frac{1}{3} \), the result is:

\[ \hat{r} = \frac{2}{3} - \frac{1}{3} \]

The bond between two sodium ions in an alkali metal crystal can be determined from the crystal equation. With the alkali, it is: 147.2 are derived from this interaction.
Example:
Calculate the enthalpy change for the reaction:

\[ \text{C}_2\text{H}_5\text{OH}(l) + \text{O}_2(g) \rightarrow \text{CO}_2(g) + \text{H}_2\text{O}(l) \]

\[ \Delta H^\circ \text{(kJ/mol)} \]

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \Delta H^\circ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_2\text{H}_5\text{OH} )</td>
<td>(-1364)</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>(0)</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} )</td>
<td>(-241)</td>
</tr>
</tbody>
</table>

\[ \Delta H^\circ = [-1364 - 12(-241)] - [-1783] = -228 \text{ kJ/mol} \]

Heat of combustion:
The enthalpy change accompanying the complete combustion of a molecule of a compound.

Organic compounds can be burnt in oxygen to form carbon dioxide and water as the sole products. (\( \text{C}_2\text{H}_5\text{OH} \) = petrol)

\( \Delta H^\circ \) is referred to the standard heat of combustion of all the substances are in their standard states.

The values for a number of familiar compounds are found in index tables. The combustion products are assumed to be solid CO\(_2\) and liquid H\(_2\)O in each case (e.g.):
The Second Law of Thermodynamics

Introduction

Something happens naturally and something doesn't (a g).}
1. Water runs downhill. (b) A gas expands to fill the available volume.
2. Heat flows down the temperature gradient. (c) A chemical reaction runs from one direction rather than another (e.g., aqueous solution of NaCl + AgNO₃ are mixed, AgCl is formed spontaneously).

This is the spontaneous direction of change that does not require work to be done to bring it about.

Question: Can we make water flow by itself upwards? Can we confine a gas to a smaller volume? Can we force some reaction to go in reverse?

Answer: No! These processes happen spontaneously; each one must be brought about by doing work (non-spontaneous processes).

All naturally occurring processes always tend to change spontaneously in a direction which will lead to equilibrium.

The Second Law of Thermodynamics summarizes these two processes.

1. It is impossible for a cyclic process to take heat from a cold reservoir and convert it into work without at the same time transferring heat from a hot to a cold reservoir.
2. It is impossible to construct a machine which is able to convey heat by a cyclic process from one reservoir at a lower temperature to another at higher temperature unless work is done on the machine by some outside agency.

The Carnot cycle

Cannot be considered a hypothetical engine which converts heat into work by a cyclic process.

Note: The cycle is a process in which a system returns to its original state after a succession of steps.
The engine consists of a cylinder fitted with a weightless and frictionless piston and containing a given weight of a working substance. Two heat reservoirs at constant temperatures $T_1$ (upper) and $T_2$ (lower) respectively are also available.

The Carnot cycle consists of four steps:

1. **Isothermal expansion**
   According to the first law:
   \[ \Delta E_1 = q_2 - W_1 \]

2. **Adiabatic expansion**
   Since no heat is transferred, $q = 0$
   According to the first law:
   \[ \Delta E_2 = -W_2 \]
3. Isothermal compression

$$\Delta E_3 = -q_1 - W_3$$

4. Adiabatic compression

$$\Delta E_4 = - W_4$$

As a result of these four stages, the system has returned to its original state.

The net change in energy for the complete cycle is:

$$\Delta E = \Delta E_1 + \Delta E_2 + \Delta E_3 + \Delta E_4$$

$$= (q_2 - W_2) - W_2 - (q_1 + W_4) + W_4$$

$$= q_2 - q_1 - (W_1 + W_2 + W_3 + W_4)$$

$$\Delta E = q_2 - q_1 - W_m$$

where, $W_m =$ net work in the complete cycle.

Since the sum of internal energy for the cyclic process is zero, then:

net work $W_m = q_2 - q_1$.

Only a portion of the heat taken in from the hot reservoir can be converted into work.

The efficiency of a machine is the fraction of heat absorbed at the higher temperature by the engine that it can convert into work.
\[ E = \frac{W_m}{q_2} = \frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2} \]

where, \( E \) = efficiency of the Carnot cycle.
\( E \) is always less than unity (\( E < 1 \)) as \( q_1 < q_2 \)

No engine can be constructed which completely convert all the heat energy applied to it into work. Also, \( E \) is determined only by \( q_1 \) and \( q_2 \) and is independent on the nature of the working substance.

**Entropy**

In order for the reaction to be reversed, the heat evolved in the original reaction would need to be completely converted into electrical energy without heating changes in other parts of the system, therefore:

All natural processes (processes occurring without external aid) are thermodynamically irreversible in nature (spontaneous).

A characteristic of spontaneous process is that they are accompanied by an increase in the disorder of the system.

The entropy can be regarded as a measure of the disorder or random arrangement of the molecules of a system. Examples:

Fusion and evaporation are both associated with an increase of entropy of the substance concerned as there is a decrease of order in each instance.

In the solid state, the atoms, ions, or molecules are arranged in a regular manner in the crystal lattice. Upon melting, most of the order is destroyed and evaporation results in a further increase of disorder.
Increase of the temperature of a gas at constant pressure and
increase of volume at constant temperature are both processes
for which the entropy of the gas is increased. In each case molecular disorder is increased.
Lowering the temperature of a solid results in a decrease of entropy as the molecules or atoms become more and more
ordered in their space lattices. At the absolute zero of temperature when the order is probably perfect, the entropy
of most pure solids is actually zero.

Entropy is the function of spontaneity. It is a state
function; i.e., it depends only on the state of a substance or system
and not on its previous history.
The increase of entropy (dS) in the course of an
infinitesimal change is equal to (dQ/T) the heat absorbed when
the change is carried out in a reversible manner divided by
the absolute temperature

\[ dS = \frac{dQ}{T} \]

The increase of entropy for a finite change in a system
between initial state and final state can be expressed as:

\[ \Delta S = S_2 - S_1 = \int \frac{dQ}{T} \]

\( S_1 \) = Actual entropy value in the initial state
\( S_2 \) = Final state

The value of \( \Delta S \) depends only on the initial and final
states of the system and not on the nature of the path.
Entropy change in a reversible process

The total entropy change of the system in a reversible process (e.g., in a Carnot cycle) must be zero since the system has returned exactly to its original thermodynamic state.

$$\Delta S = \oint \frac{dQ_{rev}}{T} = 0$$

To calculate the entropy change of systems and surroundings for a reversible isothermal process:

**Entropy change of the system is**

$$\Delta S_{\text{system}} = \frac{q}{T}$$

At the same time, the heat lost by the surroundings is $-q$

hence, the entropy change of surroundings is:

$$\Delta S_{\text{surroundings}} = -\frac{q}{T}$$

The total change of entropy during expansion is then:

$$\Delta S_{\text{expansion}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

$$= \frac{q}{T} - \frac{q}{T} = 0$$

and the total entropy change during compression is:

$$\Delta S_{\text{compression}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

$$= -\frac{q}{T} + \frac{q}{T} = 0$$
The total entropy change for the complete cycle is:

\[
\Delta S_{\text{Total}} = \Delta S_{\text{expansion}} + \Delta S_{\text{compression}} = 0
\]

**Conclusions**

In a reversible isothermal process the entropy change of the system and surroundings is always zero.

The total entropy change for a reversible isothermal cycle is zero, i.e., at the end of the cycle the system has the same entropy as it had in the initial stage.

**Entropy change in an irreversible process**

Irreversible processes are those which have a natural tendency to occur. These processes are **spontaneous**. The driving force that causes reactions to occur spontaneously is the lack of balance in these processes.

The work done by irreversible expansion is less than the work done in a reversible compression. The heat absorbed for irreversible expansion will also be less than heat absorbed for reversible expansion.

\[
W_{\text{irreversible}} < W_{\text{reversible}}
\]

Since \(\Delta S\) is a function of state (i.e., it depends on initial and final states irrespective of how the process is carried out, consisting of an ideal gas spontaneously from \(V_1\) to \(V_2\)).
given by the equation:  \[ \Delta S = R \ln \frac{V_2}{V_1} \]

For any irreversible cyclic process, the increase in entropy is due to the conversion of work into heat. Since the working substance has returned to its original state, it suffers no change of any kind. But the surroundings lost heat equal to \( q \) in the irreversible expansion and gained heat in the reversible compression. The net heat gained by the reservoir is

\[ q = q_{\text{rev}} - q \]

where \( q_{\text{rev}} = \text{heat lost} \), \( q \) = heat gained

\[ \Delta S = \left( \frac{q}{T} - \frac{q}{T_0} \right) \]

Since \( q_{\text{rev}} > q \), \( \Delta S > 0 \) and the net work on the cycle - \( W - W_m \) < 0

where:
- \( W \) = work done by the working substance (gas)
- \( W_m \) = performed on the gas by surroundings

A negative value of the net work means that work is done on the working substance, resulting in the liberation of heat which is taken by surroundings, thus causing entropy increase in surroundings. (\( \Delta S = 0 \) for reversible process \( \Delta S > 0 \) for irreversibility will occur in an increase of entropy and thus:

- The entropy of the universe is continually increasing
- According to first law of thermodynamics
- The energy of the universe is constant

According to 2nd law

- The entropy of the universe is continually increasing and tends to a maximum
Entropy changes for an ideal gas

Exercise: Calculate the entropy change of a sample of perfect gas when it expands isothermally from volume \( V_1 \) to volume \( V_2 \).

Solution: The heat absorbed \( Q \) during an isothermal expansion of a perfect gas can be derived from the first law equation:

\[ W = Q - dU \]

Since for an ideal gas \( U = \frac{1}{2} nRT \),

\[ W = \frac{1}{2} nRT \ln \left( \frac{V_2}{V_1} \right) \]

Thus, the work done for an isothermal expansion of an ideal gas from \( V_1 \) to \( V_2 \) is straightforward.

\[ W = \frac{1}{2} nRT \ln \left( \frac{V_2}{V_1} \right) \]

Exercise: Calculate the change in entropy when the volume of a perfect gas is doubled at constant temperature.
Entropy and Change of State

The entropy of a system is determined by the freedom possessed by the molecules in the system. It is considered as a measure of the disorder or random arrangement of the molecules comprising a substance and suspension are both associated with an increase in entropy of the substance concerned on these are measured under the same

In the solid state, the atoms or molecules are arranged in a regular manner within crystalline lattice. Thus, a lattice of the hard is destroyed and organization results in a further increase of the solid.

The values of boiling points, molar heat of vaporization, and entropy change per mole of some liquids are listed in the following table and

Many liquids have the value of over 100 molar
The corresponding equations for the change in energy during change in state (fission, vaporization, and melting) are given as:

\[
W = \frac{\Delta U}{\Delta T}, \quad \Delta H = \Delta U + \Delta \left( n \cdot \Delta q \right)
\]

where \( W \), \( \Delta U \), \( \Delta H \), and \( n \) are the work done, energy of reaction, energy of change, and number of moles, respectively.
The Third Law of Thermodynamics
(The determination of entropies of substances)
When a system goes from an ordered state to a disordered state, the entropy is increased. The converse is also true.
A perfectly ordered crystal at the absolute zero of temperature would then have a zero entropy value, since the atoms in a crystal are perfectly ordered and confined to one position only.

The entropy of a pure perfect crystalline substance is zero at the absolute zero of temperature.

The importance of this law that it provides the indication of absolute value of entropy of pure substance from thermal data alone.

**Example**
Consider a process involving the transformation of a substance from the stable one at temp, to a temp. of origin to melting point.
The entropy change for such a process is given by:

\[ S_f = S_i + \int_{T_i}^{T_f} \left( \frac{\Delta S}{\Delta T} \right) \, dT \]

Since for the third law, \( S_f = 0 \)

\[ S_f = S_i + \int_{T_i}^{T_f} \left( \frac{0}{\Delta T} \right) \, dT = 0 \]
Absolute entropies may be used to calculate the entropy change accompanying chemical reactions. The standard entropy change for a general chemical reaction is the difference between the molar entropies of the pure products and the pure reactants in their standard states at the specified temp.

\[ \Delta S_{\text{products}} - \Delta S_{\text{reactants}} \]

Example: Calculate the entropy change for the combustion of gasoline entropies for:

\[ \text{C}_8\text{H}_{18}(s) + \frac{25}{2} \text{O}_2(g) \rightarrow 8\text{CO}_2(g) + 9\text{H}_2\text{O}(l) \]

\[ \Delta S_{\text{combustion}} = \text{sum of product entropies} - \text{reactant entropies} \]

Note: The 3rd Law of Thermodynamics does not apply to a specific special class of substances, perfectly crystalline substances, and not to all substances.
Free energy functions

Consider a system in contact with a reservoir at temperature $T$, in which an irreversible internal process occurs and the only work done is the $P V$ work for the irreversible process. The enthalpy change of the system is

$$
\Delta H > q
$$

$q$ - quantity of heat exchanged with a reservoir.

$$
\Delta S > q
$$

$$
q > T \Delta S < 0
$$

Some work done is only $P V$ work. From the first law

$$
\Delta S = \frac{q - PV}{T}
$$

$$
q = \Delta H + PV
$$

Substituting (2) into (3)

$$
\Delta H = t \Delta S - PV
$$

Equation (4) is used because for a spontaneous change with the only work done is the $P V$ work.

If the volume and entropy of the system are held constant, equation (4) becomes

$$
(dE)_{V,S} < 0
$$

For any irreversible process in a system of constant volume and does not change its entropy, the internal energy decreases.
The volume and internal energy of a system may be

\[ -(dS)_{E,V} < 0 \]

written constant by isolating the system. Equation (9) becomes

\[ (dS)_{E,V} > 0 \]

The entropy must increase in each irreversible process

in a system of constant energy and constant volume, such as an isolated system, the equilibrium position is in the

direction of highest entropy

- System which is not isolated, there are entropy change

in the surroundings, and if the volume is constant

during the additional irreversible process, (eqn) becomes

\[ (dF - TdS)_{E,V} < 0 \]

\[ d(F - TS)_{E,V} < 0 \]

The quantity \((F - TS)\) is referred to the

Helmholtz free energy represented by \(A\)

\[ A = E - TS \]

differentiation at constant temp

\[ dA = dF - TdS \]

For a spontaneous process, equation (10) becomes

\[ (dA)_{E,V} < 0 \]

In an irreversible process at constant temp and volume,

the Helmholtz free energy \(A\) decreases
For a system at constant \( T \) and \( V \) the \( PV \) work term will be zero. The system does no other work.

\[
\text{d}A = 0 \quad \text{(13)}
\]

The condition of equilibrium for a system that can do no work is then \( \text{d}A = 0 \).

5. Physical processes and chemical reactions which are of interest are usually carried out in the laboratory at constant \( T \) and \( P \). For such processes, equation (14) can be written as:

\[
d(E + PV - TS)_{T,P} < 0 \quad \text{(4a)}
\]

The quantity \((E + PV - TS)\) is referred to as the Gibbs free energy represented by \( G \).

\[
G = E + PV - TS \quad \text{(18)}
\]

\[
G = H - TS \quad \text{(19)}
\]

and for infinitesimal change under isothermal conditions:

\[
dG = dH - TdS \quad \text{(18)}
\]

For a change at constant "\( P \)" and constant "\( T \)" and whose only mechanical work is done, the free energy is equal to the enthalpy change minus the product of absolute temperature and the entropy change. Equation (16a) can be written as:

\[
(dG)_{T,P} < 0 \quad \text{(16)}
\]

For reversible process at constant \( T \), \( G \) in which only external work done, the Gibbs free energy decreases.
\[
\begin{aligned}
(dS)_{V,N} &> 0 \\
(dE)_{S,V} &< 0 \\
(dA)_{T,V} &< 0 \\
(dG)_{T,P} &< 0 \\
(dS)_{B,V} &= 0 \\
(dE)_{S,V} &= 0 \\
(dA)_{T,V} &= 0 \\
(dG)_{T,P} &= 0
\end{aligned}
\]

Maxwell Relations

From the first law of thermodynamics:

\[
dS = \frac{q}{T} \quad \text{... (1)}
\]

From the first law:

\[
dE = q - pdV \quad \text{... (2)}
\]

Combining equations (1) & (2):

\[
[dE = T \cdot dS - \beta dV] \quad \text{... (3)}
\]

The differentials for \( H, G, A \) may also be obtained

\[
H = E + PV
\]

\[
dH = dE + PDV + VdP \quad \text{... (4)}
\]

Substituting \( dE \) from equation (2):

\[
dH = dS + PDV + \beta dV + VdP
\]

\[
dH = TdS + \beta dV \quad \text{... (5)}
\]

\[
A = E - TS
\]

\[
dA = dE - \beta dS - 3dT \quad \text{... (6)}
\]

Substitute (3) into (6).
\[ \Delta A = \int \frac{\partial A}{\partial T} \, dT - \int \frac{\partial A}{\partial V} \, dV - \int \frac{\partial A}{\partial s} \, ds - 8dT \]

\[\sqrt{\Delta A} = -8dT - \int \frac{\partial A}{\partial V} \, dV \quad \ldots \quad (7)\]

\[ G = H - TS \]
\[ \delta G = \delta H - T \delta S - S \delta T \quad \ldots \quad (8) \]

Substitute (11) in (8):
\[ \delta G = \delta E + \int \frac{\partial E}{\partial V} \, dV + \int \frac{\partial E}{\partial P} \, dP - T \delta S - S \delta T \quad \ldots \quad (9) \]

Substitute (8) in (9):
\[ \delta G = -T \delta S - \int \frac{\partial E}{\partial V} \, dV + \int \frac{\partial E}{\partial P} \, dP + \int \frac{\partial E}{\partial V} \, dV + \int \frac{\partial E}{\partial P} \, dP - S \delta T \]

\[ \delta G = -S \delta T + \int \frac{\partial E}{\partial P} \, dP \quad \ldots \quad (10) \]

The four fundamental equations of thermodynamics are:

\[ \delta E = -T \delta S - \int \frac{\partial E}{\partial V} \, dV \quad \ldots \quad (I) \]
\[ \delta H = -T \delta S + \int \frac{\partial E}{\partial P} \, dP \quad \ldots \quad (II) \]
\[ \delta A = S - \int \frac{\partial E}{\partial V} \, dV \quad \ldots \quad (III) \]
\[ \delta G = -S \delta T + \int \frac{\partial E}{\partial P} \, dP \quad \ldots \quad (IV) \]

At constant P, \( \delta P = 0 \) in equation (IV):
\[ \delta G = -S \delta T \]
\[ \int \frac{\partial G}{\partial t} \, dt = -S \quad \ldots \quad (11) \]

and \( \delta A \) constant T:
\[ \delta G = \int \frac{\partial E}{\partial P} \, dP \]
\[ \int \frac{\partial G}{\partial P} \, dP = -V \quad \ldots \quad (12) \]
For an ideal gas: \[ PV = nRT \]

For 1 mole of an ideal gas: \[ \nu = \frac{RT}{P} \]

Substituting \( \nu \) in equation (12): \[ \left( \frac{dG}{dT} \right)_P = \frac{RT}{P} \]

\[ \Delta G_2 = G_2 - G_1 = RT \int_{P_1}^{P_2} \frac{dT}{T} \]

Exercise

Calculate the change in molar Gibbs energy of a perfect gas when the pressure is increased isothermally from 1.0 bar to 2.0 bar.

At constant \( P \), \[ S = -(\frac{dG}{dT})_P \]

\[ \Delta S = S_2 - S_1 = -R \ln \frac{P_2}{P_1} \]

\[ S_2 = S_1 - R \ln \frac{P_2}{P_1} \]

Exercise

The standard entropy of \( \text{O}_2 \) at 298 K is 205.03 \( \frac{J}{K \cdot \text{mol}} \). What is the entropy at 9.1 atmospheres?

Phase Equilibria

The relationship between variables in equilibria between phases of one component (e.g., liquid and vapor, solid and vapor, solid and liquid...) can be obtained from a thermodynamic relationship.
Consider a liquid in equilibrium with its vapor at temperature $T$ and pressure $P$. At equilibrium, let the temp be changed to $T + dT$ and pressure to $P + dP$.

For liquids:
\[
(dG)_l = V dP - S dT \quad \text{(1)}
\]

For vapors of the liquids:
\[
(dG)_v = V dP - S dT \quad \text{(2)}
\]

When two phases are in equilibrium:
\[
(dG)_l = (dG)_v \quad \text{(3)}
\]

\[
V_l dP - S_{(l)} dT = V_{(v)} dP - S_{(v)} dT \quad \text{(4)}
\]

\[
\frac{dP}{dT} = -\frac{\Delta S}{\Delta V} \quad \text{(5)}
\]

$\Delta S$, $\Delta V$ = changes in entropy and volume respectively.

Again at equilibrium:
\[
\Delta G = 0
\]
\[
(\Delta G)_v = (\Delta H)_v \quad T \Delta S = 0 \quad \text{(6)}
\]

\[
\Delta S = \frac{\Delta H_v}{T} \quad \text{(7)}
\]

Substituting $\Delta S$ in eqn (5):

\[
\frac{dP}{dT} = \frac{\Delta H_v}{T \Delta V_{(v)}} = \frac{\Delta H_v}{T(V_v - V_l)} \quad \text{(8)}
\]

or
\[
\frac{dP}{dT} = \frac{\Delta H_v}{T(V_v - V_l)} \quad \text{(9)}
\]

and
\[
\frac{dP}{dT} = \frac{\Delta H_v}{T(V_v - V_l)} \quad \text{(10)}
\]
In vaporization and sublimation equations in which one of the two phases is gaseous, equations (a) and (c) can be put in a more convenient form:

\[
(\Delta V)_v = V_0 - V_g
\]

Since \( V_0 \gg V_g \)

\( V_0 \) can be neglected

\[
\Delta V = V_0 = \frac{RT}{v}
\]

\[
\frac{dP}{dT} = \frac{\Delta H_v \times P}{RT}
\]

\[
\frac{dP}{T} = -\frac{\Delta H_v}{R} \times \frac{dT}{T^2}
\]

\[
\frac{dP}{T} = \frac{\Delta H_v}{R} \int_0^T \frac{dT}{T^2}
\]

\[
\ln \frac{P_T}{P_0} = \frac{\Delta H_v}{R} \left( \frac{T_2}{T_1} \right)
\]

\text{Clausius-Clapeyron equation}

\text{Example:}

The boiling point of ether is 35.5°C at 760 mm pressure. At what temp. will it boil at a pressure of 750 mm Hg?

The latent heat of vaporization of ether = 884 cal/gm and its u. wt. = 74.
Chemical Potential

The chemical potential can be regarded as a force which drives the chemical systems to equilibrium. It can be shown that the Gibbs free energy of a system changes when a substance is added to it.

The chemical potential as a function of mole fraction \( \rho \) is equal to the rate of change of Gibbs free energy of the system with the number of moles \( \rho \). All other components other than number of moles of all other components are held constant.

\[
\mu = \left( \frac{\partial G}{\partial \rho} \right)_{T,P}
\]

For a pure substance, the Gibbs free energy is:

\[
G = \mu \cdot \rho
\]

where \( \mu \) is the Gibbs free energy.

Applying the temperature at constant \( T \):

\[
\Delta G = \mu_1 - \mu_2
\]

The chemical potential of a perfect gas at pressure \( P \) can be written as:

\[
\mu = \frac{N}{V} R T + \mu^0
\]

where \( \mu^0 \) is the standard chemical potential at the standard state. The chemical potential can be expressed in terms of activity \( a_i \) and molal concentration:

\[
\mu = \mu^0 + R T \ln a_i
\]
Chemical Equilibrium

Reversible processes

A + B ⇌ C + D

A stage of chemical equilibrium is reached when the rate of the forward reaction becomes equal to the rate of the backward reaction. In this stage, the composition of the reactants and products get fixed. Thus, chemical equilibrium is dynamic in nature:

H₂ + I₂ ⇌ 2 HI

At 155°C, the composition of the equilibrium mixture is found to be: 12% H₂, 19% I₂, and 76% HI. If the reaction is started with HI at the same temp (155°C), we shall find that the same composition persists for the equilibrium mixture.

The law of mass action

At constant temperature, the rate at which a substance reacts is directly proportional to its molar mass.

The velocity of a chemical reaction is proportional to the product of the "activity molar" of the reaction. The term "activity molar" is a thermodynamic quantity and is given by:

\[ a = C \cdot \gamma \]

where

\[ a \] = activity molar

\[ C \] = molar concentration

\[ \gamma \] = activity coefficient

For reactions involving gaseous solutions, \( \gamma = 1 \) and the concentration may be substituted for the activity.
For the general reversible reaction:

\[ A + B \rightleftharpoons C + D \]

According to the law of mass action, the rate of the forward reaction \( R_f \) is given by:

\[ R_f = k_f C_A C_B \]

\( k_f \) = proportionality constant for the forward reaction.

The rate of the reverse reaction \( R_r \) is given by:

\[ R_r = k_r C_C C_D \]

\( k_r \) = proportionality constant for the reverse reaction.

\[ C_A, C_B, C_C, C_D \] = Concentrations of \( A, B, C \) and \( D \) respectively

At equilibrium, the two rates must be equal:

\[ R_f = R_r \]

\[ k_f \frac{C_A C_B}{C_C C_D} = k_r \]

\[ \frac{C_C C_D}{C_A C_B} = \frac{k_f}{k_r} \]

\( K_e \) = equilibrium constant

The equilibrium constant is expressed in terms of concentration units, i.e., mols per liter of the various species.

For a process involving more than a single molecule of each of the reactants and products, then:

The rate is proportional to the concentration of the given substance raised to the power equal to the number of molecules of the substance participating.

\[ a \text{A} + b \text{B} \rightleftharpoons c \text{C} + d \text{D} \]
The rate laws are given by:

\[ R_1 = k_{R_1} C_A C_B \]

\[ R_2 = k_{R_2} C_A C_B \]

\[ R_1 = R_2 \quad \text{at equilibrium} \]

\[ \frac{C_A^e}{C_B^e} = k_2/k_1 = K \]

**K = dissociation**

**K = association**

Equilibrium constants expressed in different units:

For reactions involving gases, the concentration of any gas at any given temperature can be expressed in terms of its partial pressure of the reactants and products.

For the general gaseous reaction:

\[ aA + bB \rightarrow cC + dD \]

If \( P_A, P_B, P_C \), and \( P_D \) are the partial pressures of the various gaseous species at equilibrium, then:

\[ K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b} \]

**K_p** = equilibrium constant in terms of partial pressures and is constant at a given temperature.

**Le Châtelier - Brown Principle:**

If a change occurs on one of the variables, such as \( T \), \( P \) or concentration under which a system is in equilibrium, the system will adjust itself so as to counteract the effect of that change.
Application of the Law of Mass Action

Homogeneous gas phase Equilibrium:

Examples are:

\[ \text{H}_2 + \text{I}_2 \rightleftharpoons 2 \text{HI} \]
\[ \text{Cl}_2 + \text{H}_2 \rightleftharpoons 2 \text{HCl} \]

For Hydrogen-Iodine equilibrium (in terms of moles):

\[ \text{H}_2 + \text{I}_2 \rightleftharpoons 2 \text{HI} \]

\[ a \cdot \text{H}_2 \cdot \text{I}_2 \]

\[ b \cdot \text{HI} \]

\[ x \cdot \text{H}_2 \cdot \text{I}_2 \]

\[ x \cdot \text{HI} \]

\[ \text{v} = \text{volume of the system} \]

\[ \text{Initial molar concentration: } c_{\text{H}_2} = a, c_{\text{I}_2} = b, c_{\text{HI}} = 0 \]

\[ \text{Equilibrium molar concentrations: } c_{\text{H}_2} = a-x, c_{\text{I}_2} = b-x, c_{\text{HI}} = 2x \]

\[ \text{The Law of Mass Action: } K_c = \frac{c_{\text{HI}}^2}{c_{\text{H}_2} \cdot c_{\text{I}_2}} = \frac{(2x)^2}{(a-x)(b-x)} \]

\[ K_c = \frac{4x^2}{(a-x)(b-x)} \]

3. Equilibrium constant in terms of pressure:

\[ \text{Initial pressure of gases: } (a), (b), 1 \]

\[ \text{Total pressure at equilibrium: } a-x+b-x-2 \]

Total no. of gaseous moles at equilibrium:

\[ (a-x)+(b-x)+(2x) \]

\[ (a+b) \]

At equilibrium, total pressure: 1

\[ \text{From Dalton's law: partial pressure } x \cdot P, x \cdot P, \text{and } x \cdot P \]
\[ P_u = \frac{a \cdot X \cdot Y}{a + b} \cdot P, \quad P_L = \frac{b - X \cdot Y}{a + b} \cdot P, \quad P = \frac{2X/b}{2Y/b} \cdot P \]

\[ K_P = \frac{P^L}{P^U} \cdot \frac{P^R}{P^I} = \frac{(\frac{2X}{a+b}) \cdot P}{(\frac{b}{a+b}) \cdot P \cdot (\frac{b-X}{a+b}) \cdot P} \]

\[ K_P = \frac{2X \cdot (b-X)}{(a \cdot X) \cdot (b-X)} \]

\[ K_P = K_C \quad \text{and 2...} \]

Equilibrium constant remains unchanged by change of volume and pressure.

**Exercise (1)**

15 gm molecules of Hz on reaction with 55 gm molecules of I2 vapors at 298K produced 10 gm molecules of H2I. Calculate the equilibrium constant of the reaction.

**Exercise (2)**

A mixture containing 25 moles of Hz and 15 moles of I2 was heated in a constant volume at equilibrium at 298K, when 20 moles of H2I were obtained. Calculate the equilibrium constant of the reaction.
Phase Equilibria

The phase diagram
The condition of equilibrium between various forms of a substance or phases of a substance is illustrated by a diagram called a phase diagram.

- CA and CB represent the variation of vapor pressure with temperature.
- CC shows the dependence of the melting point on pressure. It may be said that two phases: (a) liquid & vapor along CA (b) solid and vapor along CB and (c) solid and liquid along CR are in equilibrium at temperatures and pressures represented by each of the curves on the diagram.

The three phases (solid, liquid & vapor) are in equilibrium at the triple point "C" where the three curves meet. There is only one point at which all three phases can exist.

In the areas between the curves there can be one phase, either solid or liquid or vapor.

(a) In the region between CA and CC only liquid exist.
(b) Region to the left of CR and BB represents BR at which solid only exist.
(c) Only vapor exist below CF and CC.
The phase rule

A phase is any homogeneous and physically distinct part of a system which is separated from the other parts of the system by definite bounding surfaces (e.g., ice & water and vapor are three phases).

A component is the smallest number of chemical constituents by means of which the composition of every phase can be expressed (e.g., The water system consists of one component and three phases (ice, water, and vapor).

Degree of freedom or Variables:
Number of variable factors such as temp, press, and conc. which need to be fixed in order that the conditions of a system at equilibrium is defined.

Systems with one, two, three, etc. degree of freedom are said to be Univariant, Divariant, Ternivariant, etc.

Phase rule
The number of degrees of freedom \( F \) of the system is related to the number of components \( C \) and phases \( P \) present at equilibrium by the equation 1:

\[
F = C - P + 2
\]

For a one component system, \( C = 1 \), \( F = 3 - P \)
or \( 1 + P = \text{?} \). The sum of the degree of freedom and the number of phases should be 3 if the system is equilibriu.
- For a system consisting of one phase only, \( P = 1 \)
  \( F = 2 \), thus two degrees of freedom (invariant).
  e.g. solid, liquid, or vapor (area under the curve).
- Temp. and press are required to specify any point in a region of the diagram.
- For a system with two phases in equilibrium, \( P = 1 \)
  \( F = 1 \) \( (2 - 2 = 0) \) (invariant).
- When three phases \( (P = 3) \) can coexist at the triple point \( T^* \), the system will have six or six degrees of freedom \( (F = 6 - 6 = 0) \) (invariant).

**Solutions:** A mixture of two or more chemically non-reacting substances whose relative amounts can vary within certain limits.

a. Homogeneous mixtures - mixtures of molecular size (e.g.,
   i. Molten mixtures
   ii. Colloidal solutions

b. Heterogeneous mixtures - e.g., (e.g.,

**Types of Solutions:** (Examples of binary system types)

1. Liquid
   - Liquid
   - Liquid

2. Liquid
   - Liquid
   - Liquid

3. Solid
   - Solid
   - Solid

4. Gas
   - Gas
   - Gas

5. Liquid
   - Liquid
   - Liquid

6. Solid
   - Solid
   - Solid

7. Gas
   - Gas
   - Gas

8. Liquid
   - Liquid
   - Liquid

9. Solid
   - Solid
   - Solid

10. Gas
    - Gas
    - Gas

11. Liquid
    - Liquid
    - Liquid

12. Solid
    - Solid
    - Solid

13. Gas
    - Gas
    - Gas

14. Liquid
    - Liquid
    - Liquid

15. Solid
    - Solid
    - Solid

16. Gas
    - Gas
    - Gas

17. Liquid
    - Liquid
    - Liquid

18. Solid
    - Solid
    - Solid

19. Gas
    - Gas
    - Gas

20. Liquid
    - Liquid
    - Liquid

21. Solid
    - Solid
    - Solid

22. Gas
    - Gas
    - Gas

23. Liquid
    - Liquid
    - Liquid

24. Solid
    - Solid
    - Solid

25. Gas
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26. Liquid
    - Liquid
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27. Solid
    - Solid
    - Solid

28. Gas
    - Gas
    - Gas

29. Liquid
    - Liquid
    - Liquid

30. Solid
    - Solid
    - Solid

31. Gas
    - Gas
    - Gas

32. Liquid
    - Liquid
    - Liquid

33. Solid
    - Solid
    - Solid

34. Gas
    - Gas
    - Gas

35. Liquid
    - Liquid
    - Liquid

36. Solid
    - Solid
    - Solid

37. Gas
Composition of solutions
Composition is the relative amount of each component in a solution.

For a binary solution of two components, A & B, where
B is the solute and A is the solvent,
- **Percentage weight:** \( \%A = \frac{w_A}{w_A + w_B} \times 100 \)
- **Weight ratio:** \( \frac{w_A}{w_B} \)
- **Percentage when d B:** \( \%A = \frac{\sqrt{d_B - 1}}{\sqrt{d_B} - 1} \times 100 \)

- **Molarity (number of moles of solute in 1 liter solution):** 
  \( M_A = \frac{n_A}{V} \)

- **Normality (number of equivalents of solute in 1 liter solution):** 
  \( N_A = \frac{n_A}{n} \)

- **Moles fraction:** \( x_B = \frac{w_B}{w_A + w_B} \)
  \( x_A + x_B = 1 \)
  \( x_B = \frac{w_B}{w_A + w_B} \)

- **Moles per volume:** 
  \( \frac{n_A}{V} \)
  \( \frac{n_A}{V} = \frac{w_A}{M} \)
  \( M_A, M_B \) are the mol of A & B.

**Exercise:**
Calculate the percentage of each component of a solution which contains 20% by volume.
Exercise:

Determine the activity of a solution containing 2.5 gms of a gas dissolved in water. Solution activity is 0.92 mole of 4.0 gms of solid in 10 liters of solution. Molar number of gas, \( M_n \) = 40 gms/liter.

Activity of gas = \( \frac{0.92 \times 40}{10} \) = 3.68 moles/liter.

Solutions of gases in liquids:

The solution of a gas in a liquid is an example of a two-component system (\( C = 2 \)) and since there are two phases (\( P = 2 \)). According to the phase rule:

\[ F = C - P + 2 = 2 - 2 + 2 = 2 \]

Thus the system is bivariant.

If the temp is kept constant, both the pressure of the gas and composition of solution (solubility of the gas) are variables. If the composition is kept constant, the pressure and Temp. are the variables.