## Thermodynamics

Thermodynamics deals with the quantitative relationships of interconversion of the various forms of energy, including mechanical, chemical, electric, and radiant energy.

- Types of Thermodynamic Systems



## 1. Open Systems

Open systems is one that freely allows energy and matter to be transferred in an out of a system.

For example boiling water without a lid Heat escape into the air. At the same time steam (which is matter) also escapes into the air.


## 2. Closed Systems

A closed system, on the other hand, does not allow the exchange of matter but allows energy to be transferred.

- It allows heat to be transferred from the stove to the water
- Heat is also transferred to the surroundings
- Steam is not allowed to escape

Example of a closed system - a pressure cooker.


## 3. Isolated Systems

This system is completely sealed.

- Matter is not allowed to be exchanged with the surroundings.
- Heat cannot transfer to the surroundings.

Example - A thermoflask is an isolated system


## The first thermodynamics law

The first law is a statement of the conservation of energy. It state that, although energy can be transformed from one kind into another, it cannot be created or destroyed. Put in another way, the total energy of a system and its immediate surroundings remains constant during any operation. The relativistic picture of the universe expressed by Einstein's equation:

$$
E=m \times c^{2}
$$

According to the first law, the effects $Q$ and $W$ in a given system during a transformation from an initial thermodynamic state to a final thermodynamic state are related to an intrinsic property of the system called the internal energy, defined as:

$$
\begin{equation*}
\Delta E=E_{2}-E_{1}=Q+W \tag{1}
\end{equation*}
$$

Where $E_{2}$ is the internal energy of the system in its final state and $E_{1}$ is the internal energy of the system in its initial state, $Q$ is the heat, and $W$ is the work. The change in internal energy $\Delta E$ is related to $Q$ and $W$ transferred between the system and its surroundings. The internal energy is related to the microscopic motion of the atom, ion, or molecules of which the system is composed. Knowledge of its absolute value would tell us something about the microscopic motion of the vibrational, rotational, and translational components. In addition, the absolute value would also provide information about the kinetic and potential energies of their electrons and nuclear element, which in practice is extremely difficult to attain.

By using equation(1) (the first law), one can evaluate the change of internal energy by measuring $Q$ and $W$ during the change of state .However, it is useful to relate the change of internal energy to the measurable properties of the system: $P, V$ and $T$ Any two of these variables must be specified to define the internal energy. For an infinitesimal change in the energy $d E$, equation (1) is written as

$$
\begin{equation*}
d E=d q+d w \tag{2}
\end{equation*}
$$

Where $d q$ is the heat absorbed and $d w$ is the work done during the infinitesimal change of the system. Capital letters $Q$ and $W$ are used for heat and work in equation (1) to signify finite changes in these quantities. The symbol d in equation (2) signifies infinitesimal changes of properties that depend on the "path," also called inexact differentials. Hence, $d q$ and $d w$ are not in these circumstances thermodynamic properties. The infinitesimal change of any state property like $d E$, also called an exact differential, can be generally written, for
instance, as a function of $T$ and $V$ as in the following equation for a closed system (i.e., constant mass):

$$
\begin{equation*}
d E=\left(\frac{\partial E}{\partial T}\right)_{V} d T+\left(\frac{\partial E}{\partial V}\right)_{T} d V \tag{3}
\end{equation*}
$$

The partial derivatives of the energy in equation (3) are important properties of the system and show the rate of change in energy with the change in $T$ at constant volume or with the change of $V$ at constant temperature. Therefore, it is useful to find their expression in terms of measurable properties. This can be done by combining equations (2) and (3) into

$$
\begin{equation*}
d q+d w=\left(\frac{\partial E}{\partial T}\right)_{V} d T+\left(\frac{\partial E}{\partial V}\right)_{T} d V \tag{4}
\end{equation*}
$$

This equation will be used later to describe properties of $E$ as a function of $T$ and $V$.

## Isothermal and Adiabatic processes

When the temperature is kept constant during a process, the reaction is said to be conducted isothermally. An isothermal reaction may be carried out by placing the system in a large constant - temperature bath so that heat is drawn from or returned to it without affecting the temperature significantly. When heat is neither lost nor gained during a process, the reaction is said to occur adiabatically. A reaction carried on inside a sealed Dewar flask or "vacuum bottle" is adiabatic because the system is thermally insulated from its surroundings. In thermodynamic terms, it can be said that an adiabatic process is one in which $d q=0$, and the first law under adiabatic conditions reduces to

$$
\begin{equation*}
d w=d E \tag{5}
\end{equation*}
$$

According to equation (5), when work is done by the system, the internal energy decreases, and because heat cannot be absorbed in an adiabatic process,
the temperature must fall. Here, the work done becomes a thermodynamic property dependent only on the initial and final states of the system.

## Work of Expansion Against a constant pressure



We first discuss the work term. Because of its importance in thermodynamics, initial focus is on the work produced by varying the volume of a system (i.e., expansion work or compression work) against a constant opposing external pressure, $P_{\text {ex }}$. Imagine a vapor confined in a hypothetical cylinder fitted with a weightless, frictionless piston of area $A$, as shown in figure (1). If a constant external pressure $P_{\mathrm{ex}}$ is exerted on the piston, the total force is $P_{e x} \times A$ because $\boldsymbol{P}=\boldsymbol{F o r c e} /$ /Area. The vapor in the cylinder is now made to expand by increasing the temperature, and the piston moves a distance $h$. the work done against the opposing pressure in one single stage is

$$
\begin{equation*}
W=-P_{e x} \times A \times h \tag{6}
\end{equation*}
$$

Now $A \times h$ is the increase in volume, $\Delta V=V_{2}-V_{1}$, so that, at constant pressure,

$$
\begin{equation*}
W=-P_{e x} \Delta V=-P_{e x}\left(V_{2}-V_{1}\right) \tag{7}
\end{equation*}
$$

## Reversible Processes

Now let us imagine the hypothetical case of water at its boiling point contained in a cylinder fitted with a weightless and frictionless piston fiq(a). The apparatus is immersed in a constant- temperature bath maintained at the same temperature as the water in the cylinder. By definition, the vapor pressure of water at its boiling point is equal to the atmospheric pressure, represented in fig(2) by a set of weights equivalent to the atmospheric pressure of 1 atm; therefore, the temperature is $100^{\circ} \mathrm{C}$. The process is an isothermal one, that is, it is carried out at constant temperature. Now , if the external pressure is decreased slightly by removing one of the infinitesimally small weights (b), the volume of the system increases and the vapor pressure fall infinitesimally. Water then a evaporates to maintain the vapor pressure constant at its original value, and heat is extracted from the bath to keep the temperature constant and bring about the vaporization. During this process, a heat exchange between the system and the temperature bath will occur.


On the other hand, if the external pressure is increased slightly by adding an infinitesimally small weight (c) the system is compressed and the vapor
pressure also rises infinitesimally. Some of the water condenses to reestablish the equilibrium vapor pressure, and the liberated heat is absorbed by the constant -temperature bath. If the process could be conducted infinity slowly so that no work is expended in supplying kinetic energy to the piston, and if the piston is considered to be frictionless so that no work is done against the force of friction, all the work is used to expand or compress the vapor. Then, because this process is always in a state of virtual thermodynamic equilibrium, being reversed by an infinitesimal change of pressure, it is said to be reversible. If the pressure on the system is increased or decreased rapidly or if the temperature of the bath cannot adjust instantaneously to the change in the system, the system is not in the same thermodynamic state at each moment, and the process is irreversible.

## Maximum Work

The work done by a system in an isothermal expansion process is at a maximum when it is done reversibly. This statement can be shown to be true by the following argument. No work is accomplished if an ideal gas expands freely into a vacuum, where $P=0$, because any work accomplished depends on the external pressure. As the external pressure becomes greater. More work is done by the system, and it rises to a maximum when the external pressure is infinitesimally less than the pressure of the gas, that is, when the process is reversible. Of course, if the external pressure is continually increased, the gas is compressed rather than expanded, and work is done on the system rather than by the system in an isothermal reversible process.

Then the maximum work done for a system that is expanded in reversible fashion is

$$
\begin{equation*}
W=\int_{1}^{2} d w=-\int_{V_{1}}^{V_{2}} P d V \tag{8}
\end{equation*}
$$

Where $P_{\text {ex }}$ was replaced by $P$ because the external pressure is only infinitesimally smaller than the pressure of the system. In similar fashion, it can
be deduced that the minimum work in a reversible compression of the system will also lead to equation (8), because at each stage $\mathrm{P}_{\mathrm{ex}}$ is only infinitesimally large than $P$. the right term in equation (8) is depicted in the shaded area in fig(), which represents the maximum expansion work or the minimum compression work in a reversible process.

## Example/ A gas expands by 0.5 liter against a constant pressure of 0.5 atm at $25{ }^{\circ} \mathrm{C}$. what is the work in ergs and in joules done by the system?

$$
\begin{aligned}
& \begin{aligned}
W & =P \Delta V \\
1 \text { atm } & =1.013 \times 10^{6} \text { dynes } / \mathrm{cm}^{2} \\
W & =\left(0.507 \times 10^{6} \text { dynes } / \mathrm{cm}^{2}\right) \times 500 \mathrm{~cm}^{2} \\
\quad & =2.53 \times 10^{6} \text { ergs }=25.3 \text { joules }
\end{aligned}
\end{aligned}
$$

The external pressure in equation(8) can be replaced by the pressure of an ideal gas, $P=n R T / V$, and by ensuring that the temperature of the gas remains constant during the change of state ( isothermal process); then one can take $n R T$ outside the integral, the equation

$$
\begin{gather*}
W_{\max }=\int d W_{\max }=-n R T \int_{V_{1}}^{V_{2}} \frac{d V}{V}  \tag{9}\\
W_{\max }=-n R T \ln \frac{V_{2}}{V_{1}} \tag{10}
\end{gather*}
$$

Note that in expansion, $\left.V_{2}\right\rangle V_{1}$, and $\ln \left(\frac{V_{2}}{V_{1}}\right)$ is a positive quantity; therefore, the work is done by the system, so that its energy decreases (negative sign). When the opposite is true, $V_{2}\left\langle V_{1}\right.$, and $\ln \left(\frac{V_{2}}{V_{1}}\right)$ is negative due to gas compression, work is done by the system, so that its energy increases (positive sign). The process itself determines the sign of W and $\Delta E$. Equation (10) gives the

maximum work done in the expansion as well as the heat absorbed, because $Q=\Delta E-W$, and, as will be shown later, $\Delta E$ is equal to zero for an ideal gas in an isothermal process. The maximum work in an isothermal revisable expansion may also be expressed in terms of pressure because, from Boyle`s law, $V_{2} / V_{1}=P_{1} / P_{2}$ at a constant temperature. Therefore, equation(10) can be written as

$$
\begin{equation*}
W_{\max }=-n R T \ln \frac{P_{1}}{P_{2}} \tag{11}
\end{equation*}
$$

Q / Calculate the final volume of one mole of an ideal gas initially at $0^{\circ} \mathrm{C}$ and 1 atm pressure. If it absorbs 2000 Cal of heat during reversible isothermal expansion. Where $V_{1}=22.4 \mathrm{dm}^{3}$, Where universal gas constant $=\mathbf{8 . 3 1 4 3}$ J/K mole

Solv./ The gas is in the standard temperature and pressure condition i.e. at S.T.P

Hence $V_{1}=22.4 \mathrm{dm}^{3}$ and $V_{2}$ have to be calculated.

As given expansion is isothermal and reversible therefore, $\Delta \mathrm{E}=0$
We know that $\quad \Delta \mathrm{E}=\mathrm{Q}+\mathrm{W}$
But $\Delta \mathrm{E}=0$
Hence $\mathrm{Q}=-\mathrm{W}=2000 \mathrm{cal}$

But 1cal=4.184 J

$$
\mathrm{Q}=2000 \mathrm{X} 4.184 \mathrm{~J}=8368 \mathrm{~J}
$$

As work done in reversible isothermal expansion is given by:

$$
\mathrm{W}=-\mathrm{nRT} \ln \left(\mathrm{~V}_{2} / \mathrm{V}_{1}\right)
$$

Therefore $\quad n R T \ln \left(V_{2} / V_{1}\right)=-W=8368 \mathrm{~J}$
$(1 \mathrm{~mol}) \mathrm{X}\left(8.314 \mathrm{~J} \mathrm{~K}^{-} \mathrm{mol}^{-}\right) \mathrm{X}(273 \mathrm{~K}) \ln \left(\mathrm{V}_{2} / 22.4 \mathrm{dm}^{3}\right)=8368 \mathrm{~J}$

$$
\mathrm{V}_{2}=242.50 \mathrm{dm}^{3}
$$

Hence the final volume of one mole of an ideal gas initially at $0^{\circ} \mathrm{C}$ and 1 atm pressure is equal to $242.50 \mathrm{dm}^{3}$.

Q/ What is the maximum work done in the isothermal reversible expansion of 1 mole of an ideal gas from 1 to 1.5 liters at $25^{\circ} \mathrm{C}$ ?

SOL//

$$
\begin{aligned}
& \mathrm{W}=-(1 \text { mole })(8.3143 \text { joules } / \mathrm{K} \text { mole })(298.15 \mathrm{~K}) \ln (1.5 / 1.0) \\
& \mathrm{W}=-1005.3 \text { joules }
\end{aligned}
$$

## Changes of state at constant volume

If the volume of the system is kept constant during a change of state, $d V=0$, the first law can be expressed as

$$
\begin{equation*}
d E=d Q_{v} \tag{12}
\end{equation*}
$$

where the subscript v indicates that volume is constant. Similarly, under these conditions the combined equation (4) is reduced to

$$
\begin{equation*}
d q_{v}=\left(\frac{\partial E}{\partial T}\right)_{v} d T \tag{13}
\end{equation*}
$$

This equation relates the heat transferred during the process at constant volume, $d Q_{v}$, with the change in temperature, $d T$. The ratio between these quantities defines the molar heat capacity at constant volume

$$
\begin{equation*}
\bar{C}_{V} \equiv \frac{d q_{v}}{d T}\left(\frac{\partial E}{\partial T}\right)_{V} \tag{14}
\end{equation*}
$$

## Ideal Gases and the First Law

An ideal gas has no internal pressure, and hence no work needs be performed to separate the molecules from their cohesive force when the gas expands. Therefore, $\mathrm{dw}=0$, and the first law becomes

$$
\begin{equation*}
d E=d q \tag{15}
\end{equation*}
$$

the process is done isothermally, there is no temperature change in the surroundings, $\mathrm{dT}=0$, and $\mathrm{q}=0$. equation (4) is reduced to

$$
\begin{equation*}
d E=\left(\frac{\partial E}{\partial V}\right)_{V} d V=0 \tag{16}
\end{equation*}
$$

In this equation , $d V \neq 0$ because has been expansion,

$$
\begin{equation*}
\therefore\left(\frac{\partial E}{\partial V}\right)_{V}=0 \tag{17}
\end{equation*}
$$

Equation (17) suggests that the internal energy of a $n$ ideal is a function of the temperature only.

## Changes of State at Constant Pressure

When the work of expansion is done at constant pressure,
$W=-P \Delta V=-P\left(V_{2}-V_{1}\right)$ by equation (7), the first law can be written as

$$
\begin{equation*}
\Delta E=Q_{P}-P\left(V_{2}-V_{1}\right) \tag{18}
\end{equation*}
$$

Where $Q_{P}$ is the heat absorbed at constant pressure.

$$
\begin{align*}
Q_{P} & =E_{2}-E_{1}+P\left(V_{2}-V_{1}\right) \\
& =\left(E_{2}+P V_{2}\right)-\left(E+P V_{1}\right) \tag{19}
\end{align*}
$$

Where $E+P V$ is called enthalpy, $\boldsymbol{H}$. By substituting $\boldsymbol{H}$ in equation (19)

$$
\begin{equation*}
Q_{P}=H_{2}-H_{1}=\Delta H \tag{20}
\end{equation*}
$$

And writing equation (18) as

$$
\begin{equation*}
\Delta H=\Delta E+P \Delta V \tag{21}
\end{equation*}
$$

For an infinitesimal change, one can write as

$$
\begin{equation*}
d q_{P}=d H \tag{22}
\end{equation*}
$$

If $\boldsymbol{T}$ and $\boldsymbol{P}$ are chosen as variables, $\boldsymbol{d H}$ can be written as

$$
\begin{equation*}
d H=\left(\frac{\partial H}{\partial T}\right)_{P} d T+\left(\frac{\partial E}{\partial P}\right)_{T} d P \tag{23}
\end{equation*}
$$

When the pressure is held constant, as, for example, a reaction proceeds in an open container in the laboratory at essentially constant atmospheric pressure, equation (23) becomes

$$
\begin{equation*}
d H=\left(\frac{\partial H}{\partial T}\right)_{P} d T \tag{24}
\end{equation*}
$$

Because $d q_{P}=d H$ at constant pressure according to equation (22), the molar heat capacity $C_{P}$ at constant pressure is define as

$$
\begin{equation*}
\bar{C}_{P}=\frac{d q_{P}}{d T}=\left(\frac{\partial H}{\partial T}\right)_{P} \tag{25}
\end{equation*}
$$

And for a change in enthalpy between products and reactants,
$\Delta H=H_{\text {products }}-H_{\text {reactants }}$, equation (25) written as

$$
\begin{equation*}
\left[\frac{\partial(\Delta H)}{\partial T}\right]_{P}=\Delta \overline{C_{P}} \tag{26}
\end{equation*}
$$

Where $\Delta \bar{C}_{P}=\left(C_{P}\right)_{\text {products }}-\left(C_{P}\right)_{\text {reactants }}$. Equation (26) is known as the Kirchhoff equation.

## Table: Modified First-Law Equations for Processes Occurring Under Various

 Conditions| Specific condition | Process | Common means for <br> establishing the condition | Modification for the first <br> law $\mathrm{dE}=\mathrm{dq}+\mathrm{dw}$ under <br> the stated condition |  |
| :--- | :--- | :--- | :--- | :--- |
| Constant heat | $d q=0$ | Adiabatic | Insulated vessel | $\mathrm{dE}=\mathrm{dw}$ |
| Reversible process <br> at constant <br> temperature | $d T=0$ | isothermal | Constant temp bath | $\mathrm{dW}=\mathrm{W}_{\max }$ |
| Constant volume | $d V=0$ | Isometric <br> (isochoric) | Closed vessel of constant <br> volume | $\mathrm{dW}=-\mathrm{pdV}=0 \mathrm{dE}=\mathrm{Qv}$ |
| Constant pressure | $d P=0$ | isobaric | Reaction occurring in an <br> open container at constant <br> atmospheric pressure | $\mathrm{dE}=\mathrm{dH}-\mathrm{Pdv}$ |

## Thermochemistry

Thermochemistry deals with the heat changes accompanying isothermal chemical reactions at constant pressure or volume, from which values of $\Delta H$ Or $\Delta E$ can be obtained.

Most chemical and physical processes of interest are carried out at constant pressure.

- A negative $\Delta H$ and $Q_{P}$ means that heat is released (exothermic).
- A positive value of $\Delta H$ and $Q_{P}$ means that heat is absorbed (endothermic).

It is also possible that a reaction takes place in a closed container; in such (i.e. $\Delta E=Q_{v}$ ).

