

CHAPTER THREE

3. Thermodynamics

Introduction

Thermodynamics is a Greek word that means, “Heat power.” It is the study of energy and its transformations. **Thermodynamics** means *flow of heat and deals with quantitative relationship between heat and other forms of energy in physic-chemical transformation*. In short, it is the study of heat, and how heat can be interconverted into other energy forms. Sometimes it is called energetic. Thermodynamics answers to *why a change occurs but not to how it occurs*. This means we never get the information about the rate of the change or the rate of reaction.

Thermodynamics has a great predicting power. It can predict whether a given process will occur spontaneously or not under a given set of conditions. The law provides necessary criteria for predicting the feasibility of a process but it gives no information with regard to the rate at which a change will proceed and makes no mention of the mechanisms of how the change is accomplished.

Thermodynamic Terms

A. System: The part of the universe selected for thermodynamic considerations (study). Based on the nature of the boundary between the system and the surrounding a system can be classified as

Open system: a system which can exchange both matter and energy with the surrounding.

Closed system: a system which exchanges energy with the surrounding but not matter.

Isolated system: a system which is devoid of any interaction with the surrounding.

Properties of a System (Extensive and Intensive)

Extensive properties: depend up on the total amount of a material in the system. For example Mass, Volume, No. of moles, Energy, Enthalpy, free energy, entropy, heat capacity.

Intensive properties: independent of the amount of the material in the system, examples of this are (molar properties such as molar volume , molar heat capacity , molar entropy), surface tension, viscosity, specific heat, thermal conductivity, density, refractive index, pressure, temperature, boiling point , freezing point and vapour pressure of liquids.

B. Surrounding: The rest of the universe outside the system which can exchange matter and energy with the system.

C. Boundary: The wall or interface between the system and surrounding with varying ability to allow the passage of matter and energy. There are different types of walls;

A permeable wall: a boundary that allows the passage of both matter and energy.

Diathermic wall: a boundary that prevents the passage of matter and allows the flow of energy

Adiabatic wall: a boundary neither allows the passage of energy nor matter.

D. The Universe: the universe comprises the system and its surrounding.

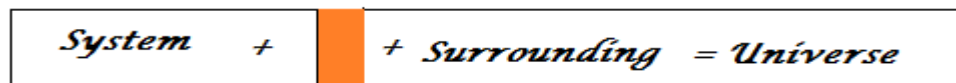


Figure 3.1. Universe, system and surrounding used in for thermodynamic considerations.

3.1.1. State of a system

State variables are various measurable properties of a system which completely define the state of a system. These variables are pressure, temperature, volume and amount or concentration. These variables are related by an equation of state for gaseous system. Change in state of a system is completely defined when the initial and final states are specified.

$$pv = nRT \quad \text{for ideal gases} \quad \text{-----} \quad (3.1)$$

$$\left(pt \frac{an^2}{v^2} \right) (v - nb) = nRT \quad \text{for Vanderwaals gases} \quad \text{-----} \quad (3.2)$$

3.1.2. Thermodynamic equilibrium, Zeroth's law of thermodynamics

Thermodynamics deals only with equilibrium states, i.e. variables of system have uniform value and constant throughout the whole system. If none of the observable properties of a system appears to change with time. The system is said to be in equilibrium. In thermodynamics three types of equilibria are observed

- i. Thermal equilibrium: if no change in temperature within the system and between the system and the surrounding
- ii. Mechanical equilibrium: if there is no unbalanced force in the interior of the system and between the system and the surrounding.
- iii. Chemical equilibrium: if no change in composition or the chemical potential of each part of the system and its surrounding must be the same.

If a system is in thermodynamic equilibrium it should satisfy the above three equilibria.

Zero law of thermodynamics

This law is known as the law of thermal equilibrium. It was put forward much after the establishment of the first law of thermodynamics. The law states that; ***“if two systems are in thermal equilibrium with other then the third system is also in thermal equilibrium with each other”***

If system A and B are separately in thermal equilibrium with another system C, then systems A and B will also be in thermal equilibrium.

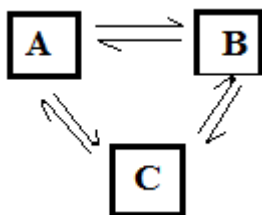


Figure 3.2. The experience summarized by the zeroth law of thermodynamics

3.1.3. Thermodynamic processes

A **process** is a change in the state of the system over time starting with a definite initial state and ending with a definite final state.

A **thermodynamic process** is defined by what happens *within* the system, in the three dimensional region up to and including the boundary, and by the forces exerted on the system by the surroundings and any external field. Types of thermodynamic process are:

1. **Isothermal process:** is a process at constant temperature of a system during various operations.
2. **Isochoric process:** is a process at constant volume of a system during various operations.
3. **Isobaric process:** is a process at constant pressure of a system during various operations.
4. **Adiabatic process:** is a process with no exchange of heat between the system and surrounding during operations.
5. **Reversible process:** is a process which doesn't deviate from equilibrium more than an infinitesimal amount. It is a process which proceeds with succession of equilibrium states. E.g., Vaporization of a liquid in a closed vessel at constant temperature and chemical reactions in galvanic cells
6. **Irreversible process:** doesn't remain in equilibrium and occurs spontaneously. All natural processes are irreversible
7. **Cyclic process:** if a system undergone a change comes back to its initial state in the process.

3.1.4. State Functions

A state function is a function that depends only on the current properties of the system and not on the history of the system. State functions are thermodynamic functions in which the changes in the values of these quantities do not depend on how the change is carried out (the path) but depends on the initial and final states of the system. Examples of state function include density, temperature, and pressure. A path function is a function that depends on the history of the system. Examples of path functions include work and heat.

State Functions;

1. A property of a system that depends only on its present state.
2. State functions are independent of the pathway taken to get to that state.
3. do not depend on what has happened in the system, or what might happen in the system in the future

For example a liter of water behind a dam has the same potential energy for work regardless of whether it flowed downhill to the dam, or was taken uphill to the dam in a bucket. The potential energy is a state function dependent only on the current position of the water, not on how the water got there. State functions can be characterized by:

- Any state functions, eg. Internal energy (U) depends only on the state, not on the path along which the system got into state. ΔU , when passing from state A to B is given by: $\Delta U = U_B - U_A$
- The differential, dU is an exact differential.
- The integral of dU about a closed path is equal to 0, i.e. $\oint dU = 0$

3.1.5. Mathematical Techniques Interconnecting the State Functions

State functions can be possible to interconnect from mathematical consideration. Consider any thermodynamic property of homogeneous system ($n = 1$) determined by: p, V and T by setting any two as independent variable; one may write as follows;

$$V = f(p, T), p = f(V, T) \text{ and } T = f(p, V)$$

Let Z be any thermodynamic or state function depend on pressure and temperature. It is written as

$$Z = f(P, T)$$

So change in Z is resulting from changes in the values of temperature and pressure is given by

$$\Delta Z = Z_{final} - Z_{initial}$$

For an infinitesimal change dZ with change in both variables can be written as

$$dZ = \left(\frac{\partial Z}{\partial P}\right)_T dP + \left(\frac{\partial Z}{\partial T}\right)_P dT$$

The dZ is exact differential which satisfies;

- 1) Euler's theorem of exactness, which is given as

$$\frac{\partial^2 Z}{\partial P \partial T} = \frac{\partial^2 Z}{\partial T \partial P}$$

- 2) The functions are single valued. This means that only one value of the dependent variable occurs for a given value of independent variable.
- 3) For the cyclic process

$$\oint dZ = 0 \quad \text{where } \oint \text{ is cyclic integral}$$

For small increase in volume, dV of $V = f(p, T)$; we can write

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT$$

To find out some unknown partial derivative, we make use of transformation formulas

- i. Suppose we want to determine the formula

$$\left(\frac{\partial V}{\partial T}\right)_P$$

Let V is constant, hence $dV = 0$

So if we rearrange the above equation, we obtain

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V$$

ii. For: $\left(\frac{\partial P}{\partial T}\right)_V$

Again using the above equation and rearranging

$$\left(\frac{\partial V}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \cancel{-\left(\frac{\partial V}{\partial P}\right)_T} \left(\frac{\partial T}{\partial P}\right)_V$$

By substituting

$$\begin{aligned}\left(\frac{\partial V}{\partial T}\right)_p &= -\left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V \\ -\left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V &= -\left(\frac{\partial V}{\partial p}\right)_T \bigg/ \left(\frac{\partial T}{\partial p}\right)_V \\ \left(\frac{\partial p}{\partial T}\right)_V &= \frac{1}{\left(\frac{\partial T}{\partial p}\right)_V}\end{aligned}$$

Example: pressure can be evaluated from ideal gas equation of one mole of gas, $PV = RT$ and so,

$$P = RT/V$$

Step 1. The change of P with change in volume at constant T can be.

$$\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial \left(\frac{RT}{V}\right)}{\partial V}\right)_T$$

Taking both R and T outside the partial derivative (they are constants) and converting it to full derivative (since it is the derivative with single variable).

$$\left(\frac{\partial P}{\partial V}\right)_T = RT \frac{d \frac{1}{V}}{dV} = RT \frac{dV^{-1}}{dV}$$

Since the derivative $\frac{dx^n}{dx} = nx^{n-1}$ the above equation become

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{V^2}$$

Step 2. The change of P with change of temperature at constant volume can be

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial \left(\frac{RT}{V}\right)}{\partial T}\right)_V$$

Taking both R and V outside the partial derivative (since they are constant) and converting it to full derivative because it is derivative with single variable. The above equation become

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} \frac{dT}{dT} \quad \dots\dots\dots 6$$

Since the derivative $\frac{dx}{dx} = 1$ so $\frac{dT}{dT} = 1$ and the above equation become

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} \quad \dots\dots\dots 7$$

Step 3. The mixed partial derivatives of equation 6 and equation 7, following the same procedures of derivative with additional rule which is $\frac{\partial^2 Z}{\partial x \partial y} = \left(\frac{\partial}{\partial y} \left(\frac{\partial Z}{\partial x}\right)_y\right)_x$ they become

$$\frac{\partial^2 P}{\partial T \partial V} = \left(\frac{\partial}{\partial T} \left(\frac{\partial P}{\partial V}\right)_T\right)_V = \left(\frac{\partial}{\partial T} \left(\frac{-RT}{V^2}\right)\right)_V = \frac{-R}{V^2} \quad \dots\dots\dots 8$$

and

$$\frac{\partial^2 P}{\partial V \partial T} = \left(\frac{\partial}{\partial V} \left(\frac{\partial P}{\partial T}\right)_V\right)_T = \left(\frac{\partial}{\partial V} \left(\frac{R}{V}\right)\right)_V = \frac{-R}{V^2} \quad \dots\dots\dots 9$$

From the above two equations, 8 and 9, indicates that dP is exact differential.

$$\frac{\partial^2 P}{\partial T \partial V} = \frac{\partial^2 P}{\partial V \partial T}$$

Therefore Pressure is state function.

Excercise: verify that density is state function from the equation $d = m/v$

3.1.6. Heat and work

Work is the motion against an opposing force. If an object is displaced through a distance dx against a force $f(x)$, then the amount of work which has to be done is

$$W = -f(x)dx \quad \text{The SI unit is Joule, J and } 1J = 1Nm$$

Work refers to the transfer of energy across the boundary caused by the displacement of a macroscopic (matter) portion of the system on which the surroundings exert a force or motion of other particles like electrons when an external force is exerted. There are different types of works. Some of them are:

1) Gravitational work ($W = -mgh$): It occurs when a body raise through a certain height against a gravitational field. Where m is mass, g is gravity which is equal to $9.81m/s^2$ and h is height.

2) Electrical work ($W = -nFE$): It occurs when a charged body is moved from one potential region to another. Where n is the number of charges (electrons) transferred, E is electromotive force and F is Faraday's constant ($F = 96,485 \text{ C}$).

3) Pressure-volume work ($W = -PdV$): A work associated with the change in volume of a system against an external pressure. It is called **mechanical work**.

N.B. We must not forget that the capacity to do work is called **Energy**: It can be

1- Kinetic energy: due to motion, $KE = 1/2mV^2$

2- Potential energy is by virtue of position: $PE = mgh$ (due to gravity)

$PE = 1/2KX^2$ (Hooks law, for springs)

$PE = -e^2/r$ (Coulomb's law, for charges)

3- Thermal energy due to temperature.

4- Chemical energy due to constitution (compositions) of the compound.

5- Nuclear energy due to nuclear constitution.

When work is done on a system by surrounding, the capacity of the system to do work is increased (i.e. energy of the system is increased). Therefore the **work done on the system is positive**. When a system does work, the energy of the system is reduced and it can do less work. The energy of a system may be changed by means other than work itself. Therefore the **work done by the system is negative**.

Internal Energy

The Internal Energy, U , of a system is an extensive thermodynamic property that measures the energy stored in a system as a result of its microscopic structure. The internal energy will include contributions from the thermal, mechanical, electrical, magnetic, chemical, and surface energies of the system. The internal energy per unit mass of the system is the specific internal energy, u .

The internal energy of a system of constant composition can be changed by work or heat interactions with its surroundings. Both of these energy transfer processes are path dependent, however, the internal energy is a function only of the state of the system.

Heat (Q)

When the energy of a system changes as a result of temperature difference between the system and its surroundings, it has been transferred as heat. It appears only during a change in the state of the system and flows from region of higher temperature to the region of lower temperature. All other forms of energy can be qualitatively converted in to work without producing changes either in the system or the surrounding but heat can't because it must be transferred with change of temperature. The common unit for measure of heat is Calorie. The relation between calorie and joule can be $1 \text{ cal} = 4.184 \text{ J}$.

From the sign convention, **Q is positive when the system absorbs heat from the surrounding and Q is negative when the system leaves heat.** Based on release or absorption of heat the process of the system can be defined as following;

An **exothermic process** is a process that releases energy as heat in to its surroundings. All combustion reactions are exothermic. Heat is negative in exothermic process.

An **endothermic process** is a process in which energy is acquired from its surroundings as heat. Heat is positive in this process. Vaporization of water is endothermic process.

Points to remember regarding heat transfer and work transfer

- a) Heat is different from other forms of energy. All others forms of energy can be quantitatively converted in to work but heat can't be completely converted in to work.
- b) In molecular terms, heat is the transfer of energy that makes use of disorderly molecular motion. The disorderly motion of molecules is called **thermal motion**. In contrast, work is the transfer of energy that makes use of organized motion.
- c) Heat transfer and work transfer are the energy interactions. A closed system and its surrounding can interact in two ways by heat transfer and work transfer.
- d) The same effect in a closed system can be brought either by heat transfer or by work transfer. Whether heat transfer or work transfer has taken place depends on what constitutes the system.
- e) Both heat transfer and work are boundary phenomena. Both are observed at the boundaries of the system and both represent energy crossing the boundaries of the system.
- f) It is wrong to say 'total heat' or heat content of a closed system, because heat or work is not a property of a system. Heat like work can't be stored by the system

=> Both heat and work are the energy in transit

- g) Heat transfer is the energy interaction due to temperature difference only. All other energy interactions may be termed as work transfer.
- h) Both heat and work are path functions and inexact transfer differentials. The magnitude of heat transfer or work transfer depends up on the path the system follows during the change of state.
- i) Heat (q) and work (w) are examples of quantities that are *not* state functions. They are not even properties of the system; instead they are quantities of energy transferred across the boundary over a period of time. It would therefore be incorrect to write " Δq " or " Δw ." Instead, they were expressed as dw and dq.

3.2. First Law of Thermodynamics

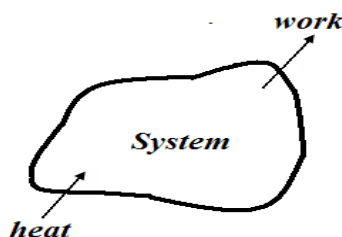
3.2.1. Introduction

The first law of thermodynamics is popularly called the law of **conservation of energy**. It states that **“Energy can be neither created nor destroyed but it may be transferred from one form into another”**. If it disappears in one form it must be reappear in some other equivalent form. It implies energy of the universe is constant.

Mathematical formulation in terms of change of internal energy, heat and work for first law is

$$\Delta U = q + W$$

If a system undergoes a change of state during which both heat transfer and work transfer are involved the net energy transfer ($q + W$) will be stored in the system.



Where $\Delta U = U_{final} - U_{initial}$ is change in internal energy, which is the total energy of the system, q is the heat absorbed by the system and W is the work done on the system (it includes all possible types of work). The above mathematical formula was proven by the following method.

Let U_1 be the initial internal energy and U_2 be the final internal energy after work done and heat. So it will be

Final energy = initial energy + heat absorbed + work done on the system

$$U_2 = U_1 + q + W$$

$$U_2 - U_1 = q + W \quad \text{Since } U_2 - U_1 = \Delta U$$

$$\Delta U = q + W$$

- If **no work is done**, $W=0$, the above equation become

$$\Delta U = q$$

It indicates the change in internal energy is equal to the heat absorbed by the system.

- For **adiabatic process (no exchange of heat)**, $q=0$, the above equation become

$$\Delta U = W$$

It indicates the change in internal energy is equal to the work done on the system

- If there is **no change in internal energy of the system**, the first law may be written as

$$q = -W$$

Thus, when the energy of the system is kept constant then heat absorbed by the system is equal to the work done by the system. In another way the above equation can be again written as

$$-q = W$$

Thus, the energy of the system kept constant and work is done on the system, then heat must flow from the system to the surroundings.

Example 4.1.

- 1) If an electric motor produces 15 KJ of energy in each second as mechanical work and lost 2KJ as heat to the surrounding, what is the change in internal energy?

$$\Delta U = -2KJ - 15KJ = -17KJ$$

Note that in the above example, -15 indicate that the energy (the capacity to do work) is produced by the electric motor; mean work is done by the motor (system).

- 2) Suppose that, when the spring was wound, 100KJ of work was done on it. But 15KJ escaped to the surroundings as heat. What is the change in internal energy of the spring?

$$\Delta U = +100KJ - 15KJ = +85KJ$$

3.2.2. Pressure-Volume Work

If the system involves gaseous substances and there is a difference of pressure between system and surrounding work is referred as **Pressure-Volume Work**. Sometimes it is called expansion-compression work. It is associated with changes in volume of the system under the action of some external pressure, P_{ext} . The increment of work exchange between system and surroundings for small fraction of the process (infinitesimal process) is denoted by ∂W .

$$\partial W = -P_{\text{ext}} dV$$

Consider a certain quantity of a gas enclosed in a cylinder fitted with a weightless and frictionless piston. The gas is held in position by a constant external pressure (P_{ext}). The force acting up on the piston is given by the product

$$F = P_{\text{ext}} \cdot A \text{ Where } A \text{ is the area of the piston (area of the cross section)}$$

We know that $\mathbf{W} = - \int \mathbf{F}(\mathbf{x})d\mathbf{x}$ from equation

$$\mathbf{W} = - \int P_{ext} \cdot A d\mathbf{x} \quad \text{where } A \cdot d\mathbf{x} = dV$$

$$\mathbf{W} = - \int P_{ext} \cdot dV$$

But dV or $\Delta V = V_f - V_i$ will have a positive value during expansion and negative value during compression. From the above equation 20, Compression leads to a positive work (work done by the surrounding) and expansion leads to negative work (work done by the system). There are four cases for this type of work, they are;

- 1) **Free expansion:** expansion against zero opposing force, $P_{ext} = 0$. Expansion of this kind occurs when a system expands in to vacuum. No work is done when a system expands freely, $w=0$.

- 2) **Expansion/compression under constant external pressure.**

Since external pressure is constant it can be taken outside the integral sign.

$$W = -P_{ext} \int_{V_1}^{V_2} dV = -P_{ext} (V_2 - V_1)$$

$$\mathbf{W} = - P_{ext} \cdot \Delta V$$

- 3) **Reversible expansion/ compression/**

When external pressure is equal to the pressure of a gas, $P_{ext} = P_{gas} = P$. This means when the system is in mechanical equilibrium. So the equation become

$$W = - \int_{V_1}^{V_2} P_{ext} dV = W = - \int_{V_1}^{V_2} P dV$$

$$\mathbf{W} = - P \cdot \Delta V$$

- 4) **Isothermal reversible expansion/compression/**

For ideal gas, a system is in thermal contact with its surrounding (which may be constant temperature bath). The reversible isothermal expansion/compression work become

$$W = - \int_{V_1}^{V_2} P dV$$

Since $PV = nRT$

$$W = - \int_{V_1}^{V_2} \frac{nRT}{V} dV$$

Since temperature is constant, the above equation become

$$W = -nRT \int_{V_1}^{V_2} \frac{dV}{V}$$
$$W = -nRT \ln \frac{V_2}{V_1}$$

When $V_2 > V_1$, $W < 0$, the system has done work on the surrounding and the internal energy is decreased. So it is expansion work. In terms of pressure, this above equation become

$$W = -nRT \ln \frac{P_1}{P_2}$$

Examples: Calculate the work done when 50g of iron reacts with hydrochloric acid in

- a) A closed vessel of fixed volume b) An open beaker at 25 °C under constant pressure.

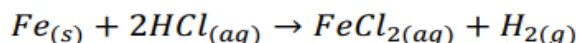
Solution

a) If there is no change in volume no expansion/compression work is there in the system, $W = 0$, because the volume is fixed (constant), $V_2 = V_1$. So the change in volume, $\Delta V = V_2 - V_1 = 0$

b) A general feature of process in which a condensed phase (solid or liquid) changes in to a gas is that the volume of the former may usually be neglected relative to that of the gas it forms. So the change in volume is approximately the same with the volume of gas formed during the reaction and it become

$$\Delta V = V_f - V_i \approx V_f = \frac{nRT}{P_{ext}}$$

Where n is the amount of H_2 produced during reaction. Let us see the chemical equation of the reaction.



$$W = -P_{ext}\Delta V = -P_{ext} \times \frac{nRT}{P_{ext}} = -nRT$$

From the above chemical equation, 1 mole H_2 is generated when 1 mole Fe is consumed and n can be taken as the amount of Fe atoms that react. The amount of Fe is calculated from the given mass and molar mass of iron (since mole, $n = m/M$)

$$W = -\frac{50g}{55.85gmol^{-1}} \times 8.314JK^{-1}mol^{-1} \times 298K = -2.2 KJ$$

3.2.3. Enthalpy (Heat content)

The change in internal energy is not equal to the energy transferred as heat when the system is free to change its volume. As a result of the energy supplied as heat to the system is returned to the surroundings as expansion work. In this case the energy supplied as heat at constant pressure is equal to the enthalpy. What is the enthalpy?

Enthalpy is defined as the sum of the internal energy and the product of pressure and volume. Mathematically it is;

$$H = U + PV$$

Since U, P, and V are all state functions, the enthalpy is a state function too and all the three quantities are extensive properties again the enthalpy is also extensive property. For change in the state of the system

$$\Delta H = \Delta(U + PV) = \Delta U + \Delta PV + P\Delta V$$

From the first law of thermodynamics

$$\Delta U = q + W = q - P\Delta V$$

And substitute for ΔU

$$\Delta H = (q - P\Delta V) + (\Delta PV + P\Delta V)$$

$$\Delta H = q + V\Delta P$$

When pressure is constant, and the above equation become

$$\Delta H = q \quad \text{Or} \quad \Delta H = q_p$$

This equation shows the change in enthalpy is equal to the energy supplied as heat at constant pressure.

- ❖ When heat is absorbed by the system at constant pressure its enthalpy is increased so ΔH is positive and the process is **endothermic process**.
- ❖ When heat is liberated by the system at constant pressure the enthalpy is decreased and ΔH is negative. So the process is **exothermic Process**.

The device used for measuring energy transferred as heat is called **calorimeter**. **Calorimetry** is the study of heat transfer during physical and chemical process. Internal energy is measured by using a **bomb calorimeter**, and then it is converted to ΔH . If a process is only involves solids or liquids the values of ΔH and ΔU are almost identical.

The enthalpy of a perfect gas (ideal gas) is related to its internal energy by

$$H = U + PV = U + nRT$$

- ▶ This equation is obtained from ideal gas equation which is $PV = nRT$
- ▶ The change in enthalpy of a reaction produces or consumes gas is

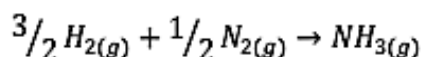
$$\Delta H = \Delta U + \Delta n_g RT$$

☞ Δn_g is change in the amount of gas molecules in the reaction; i.e. the difference of the sum of the amount of gas molecule in the product and the sum of the gas molecule in the reactant.

Factors affecting enthalpy of reaction

- ❖ Physical state of reactants and products
- ❖ Allotropic forms of elements involved in the reaction
- ❖ Chemical composition of reactants and products
- ❖ Amount of reactants
- ❖ Temperature

Example: The enthalpy change accompanying the formation of 1 mol of $\text{NH}_{3(g)}$ from its elements at 298K is -46.1KJ. Estimate the change in internal energy. The chemical equation is



The change in the amount of gas phase molecule is

$$\Delta n_g = 1.00\text{mol} - 1.50\text{mol} - 0.50\text{mol} = -1.00\text{mol}$$

$$\Delta U = \Delta H - 1.00\text{mol} \times RT = -43.6\text{kJ}$$

Problem: e

3.2.4. Heat Capacity

Two metals at the same temperature have not necessarily received the same amount of heat energy. This is due to their heat capacity. **Heat capacity** is the amount of heat required to raise the temperature of a system by one degree Celsius or the ratio of heat absorbed for the resulting increase in temperature. In another way the above definition indicates that it is a measure of the ability of the material to absorb thermal energy. In molecules, **thermal energy** is the sum of the kinetic energy of atomic motions and the potential energy of distortion of interatomic bonds. Mathematically it can be represented as

$$C = \frac{dq}{dT}$$

From the first law of thermodynamics

$$q = \Delta U - W \text{ and } q = \Delta U + P\Delta V$$

So the heat capacity become

$$C = \frac{dU + PdV}{dT}$$

At constant volume, $dV = 0$, the above equation become

$$C_v = \frac{q_v}{dT} = \left(\frac{\partial U}{\partial T} \right)_v = \frac{\Delta U}{\Delta T}$$

- **C_v is the heat capacity at constant volume** gives the **rate of change of internal energy with temperature** at constant volume. Sometimes, it is called **isochoric heat capacity**. At constant pressure the heat capacity become

$$C_p = \frac{q_p}{dT} = \left(\frac{\partial U}{\partial T} \right)_p + P \left(\frac{\partial V}{\partial T} \right)_p$$

Since, $H = U + PV$, differentiating the above equation with respect to T at constant pressure gives

$$\left(\frac{\partial H}{\partial T} \right)_p = \left(\frac{\partial U}{\partial T} \right)_p + P \left(\frac{\partial V}{\partial T} \right)_p$$

So the right hand side term of this equation is the same with the right hand side term of previous equation C_p of heat capacity at constant pressure. Therefore the left hand side of the equation is also equal.

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p = \frac{\Delta H}{\Delta T}$$

C_p is the heat capacity at constant pressure and it is the rate of change of enthalpy with temperature at constant pressure. Sometimes, the heat capacity at constant pressure is called **isobaric heat capacity**.

- ▶ **Molar heat capacity (C_p and C_v)** is a measure of the amount of heat necessary to raise the temperature of one mole of a pure substance by one degree K.
- ▶ **Specific heat capacity (c_p and c_v)** is a measure of the amount of heat necessary to raise the temperature of one gram of a pure substance by one degree K.

NOTE:

- ▶ C_p is always greater than C_v. The difference between C_p and C_v is very small for Solids and liquids, but large for gases. For n moles of ideal gas they are called molar heat capacities.

$$C_v = \frac{C_v}{n} \text{ and } C_p = \frac{C_p}{n}$$

- The difference for n moles of ideal gas is

$$C_p - C_v = nR$$

For a one-phase system of mass *m*, the **specific heat capacity at constant pressure**, c_p is

$$c_p = \frac{C_p}{m}$$

The adjective **specific** means “divided by mass, m.” so the specific heat capacity become

$$c = \frac{\Delta Q}{m\Delta T}$$

Table 3.1. Specific heat capacity and heat capacity of some substances

Substance	Air	Al	Cu	Au	Fe	Hg	NaCl	Ice	Water
c (J/g °C)	1.01	0.902	0.385	0.129	0.450	0.140	0.864	2.03	4.179
C (J/°C) for 100 g	101	90.2	38.5	12.9	45.0	14.0	86.4	203	417.9

Example: The heat capacity C_p of 1.500 mole of F₂ is 46.95 J.K⁻¹ at 25 °C. Assume the gas is ideal and calculate the molar heat capacity F₂ gas at constant volume, C_v.

Solution: 1st Find the molar heat capacity at constant pressure

$$C_{p,m} = C_p/n = (46.95 \text{ J.K}^{-1}) / (1.500 \text{ mol}) = 31.30 \text{ J.K}^{-1} \cdot \text{mol}^{-1}$$

Then the next will be finding the heat capacity at C_v from the relationship between the C_p. Therefore it is

$$C_v = C_p - R = (31.30 - 8.31451) \text{ J K}^{-1} \text{ mol}^{-1} = 22.99 \text{ J K}^{-1} \text{ mol}^{-1}$$

3.3. Thermochemistry

Thermochemistry is the branch of physical chemistry deals with the heat change during chemical or physical process. Heat is either absorbed or evolved during transformation. Since heat is depends on the path of the reaction, it is more convenient to express the energy of the system in terms of thermodynamic quantities as they are independent of path. The energy changes in chemical reactions are due to bond breaking and formation of new bonds.

Enthalpy of reaction: is the amount of heat absorbed or evolved in the transformation of reactant at a given temperature and pressure in to products at the same temperature and pressure. Example



Enthalpy of the reaction depends up on the conditions under which thermochemical reactions are carried out. The conditions are listed below with brief explanations.

1) At constant volume: when the reaction carried in closed and rigid container.

The 1st law of thermodynamics becomes, $\Delta U = q_v$ but

$$\Delta U = \sum U_{product} - \sum U_{reactant}$$

This equation indicates that *the enthalpy change of a reaction at constant volume is exactly equal to change in internal energy or the thermal change that occur in chemical reaction due to the difference in the sum of internal energy of products and the sum of internal energy of reactants.*

2) At constant pressure: the system is either kept open to the atmosphere or confined within the vessel in which a constant external pressure is exerted. If w is pressure-volume work only, from the first law of thermodynamics,

$$q_p = \Delta U + W = \Delta U + P\Delta V$$

From the above equation

$$q_p = \left(\sum U_P - \sum U_R \right) + P(V_P - V_R)$$

Collecting the like terms, terms of product and reactant together, then the above equation become,

$$q_p = \left(\sum U_P + PV_P \right) - \left(\sum U_R + PV_R \right)$$

Since $H = U + PV$ the above equation become

$$q_p = \sum H_P - \sum H_R$$

So the difference in the enthalpy of the product and the reactant is the change in enthalpy of the system. Therefore,

$$q_p = \Delta H$$

But the enthalpy change is

$$\Delta H = \Delta U + P\Delta V$$

$$\Delta H = \Delta U + [PV]_{product} - [PV]_{reactant}$$

For the system involving liquid and solid the volume of reactant equal to the volume of product, so

$$\Delta H = \Delta U$$

For gases (ideal gas, $PV = nRT$), ΔH become

$$\Delta H = \Delta U + [nRT]_{product} - [nRT]_{reactant}$$

Taking constants as common, since the temperature is the same for product and reactant, the above equation become

$$\Delta H = \Delta U + RT(n_p - n_R)$$

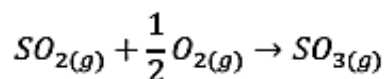
$$\Delta H = \Delta U + \Delta nRT$$

From equation 40 and 48, the above equation can be written as

$$q_p = q_v + \Delta nRT$$

Example

- 1) For conversion of a mole of $SO_{2(g)}$ in to $SO_{3(g)}$ the internal energy of reaction at constant volume at 298K is -97.027KJ. Calculate the enthalpy of a reaction at constant pressure. The reaction is



Solution

$$\text{From the above } \Delta n = n_p - n_r = 1 - \left(1 + \frac{1}{2}\right) = -\frac{1}{2}$$

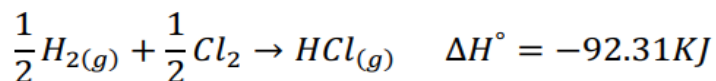
$$\Delta H = \Delta U + \Delta nRT = (-97.02\text{kJmol}^{-1})\left(-\frac{1}{2}\right)(RT)$$

$$\Delta H = -98.267\text{KJmol}^{-1}$$

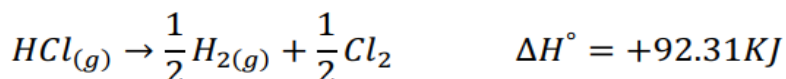
The Law of Thermochemistry

1. **Lavoisier or Laplace law:** the quantity of heat required for the decomposition of a compound in to its elements must be equal to the heat evolved during the formation of a compound from its element.

In this time thermochemical equations can be reversed and the sign of ΔH° is changed.



May be written as

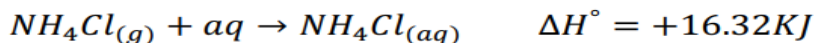
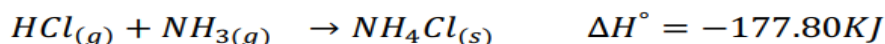


2. **Hess's Law:** states that standard enthalpy of overall reaction is the sum of the standard enthalpies of the individual reactions in to which a reaction may be divided.

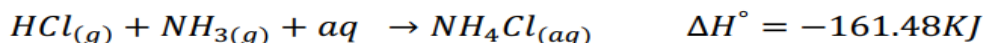
Example:

- 1) Consider formation of an aqueous solution of ammonium chloride from gaseous hydrochloric acid and ammonia.

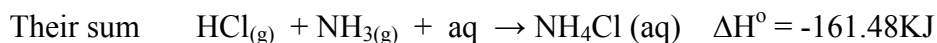
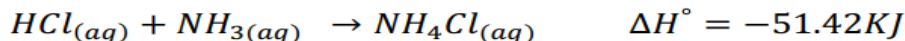
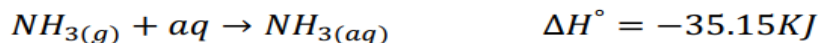
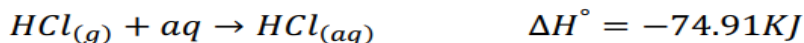
Case1;



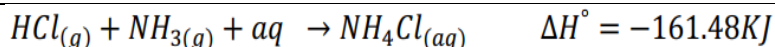
Their sum



Case2:



Their sum



3.4. Second Law of Thermodynamics

The first law enable us to compute and for different chemical reaction and physical transformations. It **is not capable of predicting the direction of a process**. So the second law was developed for prediction of the direction of the process (reaction).

The important term of indicating the direction of the in the 2nd law of thermodynamics is

Spontaneous process which is a process that takes place without the intervention of external force.

All process take place in nature are spontaneous in character.

This means they only proceed in one direction and therefore **they are thermodynamically irreversible**.

Some of the statements of the 2nd law of Thermodynamics are;

- 1) Entropy increases in irreversible process.
- 2) Heat cannot pass from a colder body to a warmer body.
- 3) Heat cannot be completely converted in to work without leaving changes either in the system or in the surrounding.
- 4) It is impossible to construct a machine working in a cycle which will transfer heat from a lower temperature to a higher temperature without the aid of external force. Such a machine is called perpetual motion machine of second order.

The first law of thermodynamics tells us that energy can be changed from one to another but can be neither created nor destroyed in any process. This law however, tells us nothing about the direction a process will take, yet we know that there are particular directions in which natural processes occur. The purpose of this topic is to explain the origin of the driving force and direction of physical and chemical changes (processes). If we wish to understand the direction of physical and chemical processes, we must have a thermodynamic function that allows us to predict the direction of the change that can be expected if we specify the initial conditions of a system and the constraints imposed on it. The energy function cannot help us, since it always remains constant in any isolated system or in the universe as a whole. Isolated systems change spontaneously from non-equilibrium state toward equilibrium states. We want a function that changes and stays constant when the system rests at equilibrium.

3.4.1. The Carnot cycle

It is reversible cycle (an ideal hypothetical cycle) in which all the processes constituting the cycle are reversible. The extent to which work can be obtained heat and its dependence on the temperature of the source and sink is given by Carnot cycle. The Carnot heat engine consists of a cylinder fitted with an ideal piston and contains a mole of an ideal gas as a working substance (system).

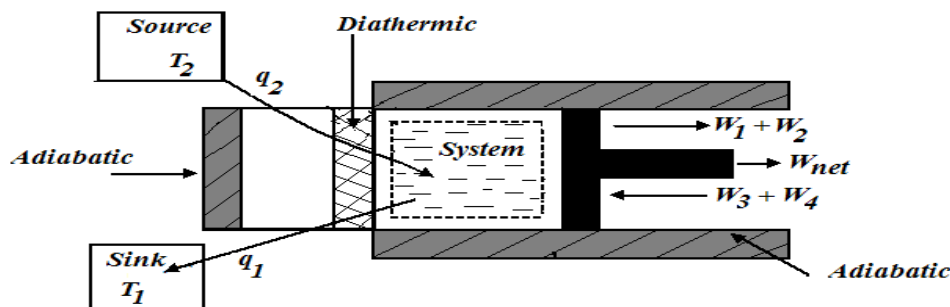


Figure 4.5. The Carnot heat engine system

The cycle consists of the following successive processes

- A reversible isothermal process (expansion)
- A reversible adiabatic process (expansion)
- A reversible isothermal process (compression)
- A reversible adiabatic process (compression)

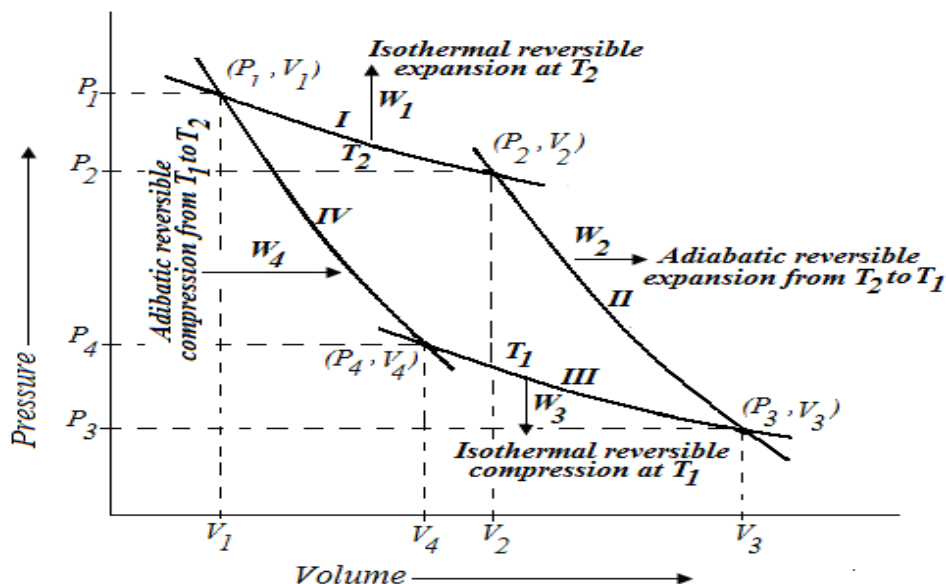


Figure 4.6. The PV diagram of Carnot heat engine system

- a) **A reversible isothermal process:** The cylinder containing the gas is placed in contact with the reservoir at T_2 . It absorbs a certain quantity of heat Q_2 and the gas is allowed to expand isothermally and reversibly at a temperature T_2 of the source.

The volume of the gas changes from V_1 to V_2 . Since $dT = 0 \Rightarrow dE_1 = 0 \Rightarrow \Delta E_1 = 0$

$$-q_2 = W_1 = -nRT_2 \ln\left(\frac{V_2}{V_1}\right) \quad \text{But } n = 1$$

- b) **A reversible adiabatic process:** The cylinder is removed from the source, it is surrounded by an adiabatic cover and the gas is allowed to expand reversibly and adiabatically from V_2 to V_3 until the temperature drops to T_1 (the temperature of the sink)

$q_2 = 0$ because adiabatic

$$W_2 = \Delta E_2 = \int_{T_2}^{T_1} C_V dT = C_V(T_1 - T_2) \quad \text{Where } W = \text{negative because } T_2 > T_1 \text{ expansion.}$$

- c) **A reversible isothermal process:** The thermal insulation is removed and the cylinder is kept in contact with the sink at T_1 . The gas is compressed isothermally and reversibly at a temperature of T_1 (sink). The volume changes from V_3 to V_4 as shown by the isotherm.

$$\Delta E_3 = 0$$

$$\Rightarrow W_3 = -q_3 = -nRT_1 \ln\left(\frac{V_4}{V_3}\right)$$

- d) **A reversible adiabatic compression process:** The cylinder is removed from the sink and surrounded by an adiabatic cover and the gas is compressed adiabatically and reversibly until its temperature rises to that of the source and the volume decreases from V_4 to V_1 .

$$Q = 0$$

$$W_4 = \Delta E_4 = \int_{T_1}^{T_2} C_V dT = C_V(T_2 - T_1)$$

The network done during the complete cycle is given by

$$W_{net} = W_1 + W_2 + W_3 + W_4$$

$$= -RT_2 \ln\left(\frac{V_2}{V_1}\right) + C_V(T_1 - T_2) - RT_1 \ln\frac{V_4}{V_3} + C_V(T_2 - T_1)$$

$$= -RT_2 \ln\left(\frac{V_2}{V_1}\right) - RT_1 \ln\left(\frac{V_4}{V_3}\right) + C_V(T_2 - T_1) - C_V(T_2 - T_1) \quad W_T = -RT_2 \ln\frac{V_2}{V_1} - RT_1 \ln\frac{V_4}{V_3}$$

Since for adiabatic expansion or compression relationship between temperature & volume is

$$T_2 = T_1 \left(\frac{V_1}{V_2} \right)^{\gamma-1} = T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1}$$

Based on this V_2 and V_3 lie on the adiabatic I and V_1 and V_4 lie on adiabatic II therefore.

$$\Rightarrow T_2 V_2^{\gamma-1} = T_1 V_3^{\gamma-1} \text{ and } T_2 V_1^{\gamma-1} = T_1 V_4^{\gamma-1}$$

$$\Rightarrow \frac{T_2 V_2^{\gamma-1}}{T_2 V_1^{\gamma-1}} = \frac{T_1 V_3^{\gamma-1}}{T_1 V_4^{\gamma-1}} \Rightarrow \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

$$W_T = -RT_2 \ln \frac{V_2}{V_1} + RT_1 \ln \frac{V_3}{V_4}, \text{ Since } -\ln \frac{V_4}{V_3} = \ln \frac{V_3}{V_4}$$

$$= -RT_2 \ln \frac{V_2}{V_1} + RT_1 \ln \frac{V_2}{V_1} \Rightarrow \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

$$W_T = (T_1 - T_2) R \ln \frac{V_2}{V_1} = -R \ln \frac{V_2}{V_1} (T_2 - T_1)$$

Efficiency of the heat engine $\frac{(-W_{\text{output}})}{q_{\text{input}}} = \frac{(-W_T)}{q_2}$

$$\eta = \frac{(-W_T)}{q_2} = R \frac{(T_2 - T_1) \ln \frac{V_2}{V_1}}{RT_2 \ln \frac{V_2}{V_1}} \quad W_1 = q_2, \text{ but opposit in direction}$$

$$\eta = \frac{(-W_T)}{q_2} = \frac{R(T_2 - T_1)}{RT_2} = \frac{T_2 - T_1}{T_2}$$

$$\eta = \frac{T_2 - T_1}{T_2} = 1 - \frac{T_1}{T_2}$$

This equation gives the efficiency of any reversible engine working between the temperatures of the source and the sink and it depends only on the temperature difference of the two and is independent of the nature of the working system or substance.

For complete conversion $\eta = 1 \Rightarrow$ either $T_2 = \infty$ or $T_1 = 0$ but both these temperatures cannot be realized in actual practice “Heat cannot be transformed completely into work”

Carnot's Theorem

- It states that of all heat engines operating between a given constant temperature source and a given constant temperature sink, none has a higher efficiency than a reversible engine.
- All reversible engines operating between the same two temperatures of the source and sink are equally efficient.

Example. A reversible heat engine working between 273K and 373K absorbs 764J of heat from the source. Calculate a) the work done b) the heat given off to the sink c) the η , and what would have been the efficiency if the temperature of the source were 573K.

Solution

$$\begin{aligned} \text{a) } \eta &= \frac{W}{q_1} = \frac{T_2 - T_1}{T_1} \Rightarrow W = q \left(\frac{T_2 - T_1}{T_2} \right) \\ &= 746J \left(\frac{100K}{373K} \right) \\ W &= \underline{\underline{200J}} \end{aligned}$$

b) heat given to the sink = $746 - 200J = \underline{\underline{546J}}$

$$\text{c) } \eta = \frac{W}{q} = \frac{T_2 - T_1}{T_2} = \frac{100K}{373K} = \underline{\underline{0.268}}$$

If the temperature of the source raised to 573K

$$\eta = \frac{573K - 273K}{573K} = \underline{\underline{0.349}}$$

Example: Liquid helium boils at about 4K and liquid hydrogen boils at about 20K. What is the efficiency of a reversible engine operating between heat reservoirs at these temperatures? For the same efficiency calculate the temperature of the hot reservoir if the temperature of cold reservoir is 350K.

Solution

$$\text{a) } \eta = \frac{20 - 4}{20} = 0.8 = 80\% \quad \text{b) } 0.8 = \frac{T - 350}{T} \Rightarrow T = 1750K$$

3.4.2. Entropy

Entropy is a measure of the randomness or disorderness in a molecular system. Sometimes, it is a measure of unavailable energy. Random motion is considered as unavailable energy. For any substance

$$S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$$

Entropy is the heat absorbed reversibly divided by the temperature.

$$dS = \frac{dQ_{\text{rev}}}{T}, \quad dQ_{\text{rev}} = TdS$$

The entropy for the temperature converted to T1 to T2 and V1 to V2 the change in entropy can be

$$\Delta S = C_V \ln \left(\frac{T_2}{T_1} \right) + nR \ln \left(\frac{V_2}{V_1} \right)$$

3.4.2.1. The combined law of the first and the second law of thermodynamics

From the first law of thermodynamics $\Delta U = q + W$

If only PV work is considered

$$q = \Delta U + P\Delta V$$

Since

$$q_{rev} = TdS, \text{ and then } TdS = dU + PdV \text{ or}$$

$$\Delta U = TdS - PdV$$

3.4.2.2. The enthalpy and the entropy relation

We know that

$$H = U + PV$$

or

$$\Delta H = d(U + PV) = dU + dPV + PdV$$

Where

$$TdS = dU + PdV,$$

$$\Delta H = TdS + VdP$$

The total entropy for isolated universe is

$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{surrounding}$$

Entropy change of a system in a reversible isothermal change can be calculated using the relation $dS = \frac{dq_{rev}}{T}$, but this equation can't be used to as such to calculate the entropy of irreversible changes.

For the surrounding entropy can be calculated if we know the gain or lose in the heat of the surrounding using the relation

$$dS = \frac{dq_{rev}}{T}$$

$$\Delta S_{surrounding} = -\frac{q_{system}}{T} = \frac{q_{surr}}{T}$$

- ◆ For reversible isolated process the change of entropy is Zero.
- ◆ For irreversible isolated process the entropy change is greater than zero.
- ◆ Entropy change for isothermal reversible process ($\Delta U = 0$ because $dT = 0$)

$$\Delta S_{sys} = nR \ln \left(\frac{V_2}{V_1} \right) = nR \ln \left(\frac{P_1}{P_2} \right) = -nR \ln \left(\frac{P_2}{P_1} \right)$$

$$\Delta S_{sys} = -2.303nR \log \left(\frac{P_2}{P_1} \right)$$

For surrounding

$$\Delta S_{surr} = -\Delta S_{sys} = -nR \ln \left(\frac{V_2}{V_1} \right) = -nR \ln \left(\frac{P_1}{P_2} \right) = nR \ln \left(\frac{P_2}{P_1} \right)$$

$$\Delta S_{surr} = 2.303nR \log \left(\frac{P_2}{P_1} \right)$$

Examples:

1. A typical resting person heats the surroundings a rate of about 100 W. estimate the entropy you generate in the surroundings in the course of a day at 20 °C.

Solution

From the relation 1J=1JS⁻¹ and there are 86400 s in the course of the day

$$q_{surr} = 86400s \times 100 \text{ JS}^{-1} = 8640000 \text{ J}$$

$$\Delta S_{surroundings} = \frac{q_{surr}}{T} = \frac{8640000}{293 \text{ K}} = +2.95 \times 10^4 \text{ JK}^{-1}$$

2. Calculate the entropy change when 1 mole of an ideal gas expands reversibly from initial volume of 1 dm³ to final volume of 10 dm³ at constant temperature of 298 K.

Solution

$$\Delta S_{sys} = nR \ln \left(\frac{V_2}{V_1} \right) = 2.303nR \log \left(\frac{V_2}{V_1} \right)$$

$$\Delta S_{sys} = 2.303(1\text{mol})(8.314\text{JK}^{-1}\text{mol}^{-1})\log 10$$

$$\Delta S_{sys} = 19.15 \text{ JK}^{-1}$$

$$\Delta S_{surr} = -\Delta S_{sys} = -19.15 \text{ JK}^{-1}$$

➤ **For adiabatic reversible process**

$$Q_{rev} = 0 \quad dS = \frac{dQ_{rev}}{T} = 0$$

This process is **isoentropic**.

➤ **Entropy change at constant volume(isochoric process) is**

$$\Delta S_v = C_v \ln \left(\frac{T_2}{T_1} \right)$$

$$\Delta S_v = \int_{T_1}^{T_2} \frac{C_v dT}{T} = C_v \ln \left(\frac{T_2}{T_1} \right)$$

$$\Delta S_v = nC_{v,m} \ln \left(\frac{T_2}{T_1} \right)$$

➤ **Entropy change at constant pressure**

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p dT}{T} = C_p \ln \left(\frac{T_2}{T_1} \right)$$

$$\Delta S_p = nC_{p,m} \ln \left(\frac{T_2}{T_1} \right)$$

Important points about the entropy change of reaction

1. Entropy increases as one goes from a solid to a liquid, or more dramatically, a liquid to a gas.
2. Entropy increases if a solid or liquid is dissolved in a solvent.
3. Entropy increases as the number of particles(molecules) in a system increases

For individual molecules $N_2O_{4(g)}(S^\circ = 304 J/K) \rightarrow 2NO_{2(g)}(S^\circ = 480 J/K)$

4. The entropy of any material **increases with increasing temperature.**
5. The entropy **increases as the mass of the molecule increases.**

$$Cl_{(2)(g)}(S^\circ = 165 J/K) > F_{(2)(g)}(S^\circ = 158 J/K)$$

6. Entropy is higher **for weakly bonded compounds than for compounds with very strong covalent bonds**

$$graphite(S^\circ = 5.7 J/K) > diamond(S^\circ = 2.4 J/K)$$

Entropy of reaction is

$$\Delta S_{rxn}^\circ = \sum nS_{(product)}^\circ - \sum nS_{(reactant)}^\circ$$

3. Free Energy Functions

In most chemical processes neither the energy nor the entropy are held constant. It becomes essential to introduce two new functions involving energy and entropy. These functions are

- ❖ Helmholtz free energy function (work function)(A)
- ❖ Gibbs free energy functions (thermodynamic potential)(G)

We know energy can be converted in to work. The portion of energy which can be converted in to useful work is termed as available energy while the remaining portion of energy which can't be converted in to useful work is known as unavailable energy.

$$\text{Total energy} = \text{isothermally available energy} + \text{isothermally unavailable energy}.$$

Since entropy is a measure of unavailable energy, when it is multiplied by temperature (TS) gives unavailable amount of heat or energy which can't be converted in to work.

Out of the total heat absorbed by the system (q), TS will give the available amount of heat which can be converted in to useful work. Thus the available energy X can be written as

$$X = q - TS$$

i) When heat is absorbed at constant volume $q_v = E$, so if X is replaced by the isothermally available energy at constant volume A which is called the **Helmholtz free energy** can be written as $A = E - TS$ or $\Delta A = \Delta E - T\Delta S$

ii) When heat is absorbed at constant pressure $q_p = H$, so if X is replaced by the isothermally available energy at constant pressure G which is called the **Gibb's free energy** can be written as

$$G = H - TS \quad \text{Or} \quad \Delta G = \Delta H - T\Delta S$$

Generally none of $\Delta H, \Delta E$ or ΔS_{system} alone decide the direction of a spontaneous process if we focus our attention on the system only. But ΔS_{univ} is a quantity which certainly decides the direction of a process.

In all spontaneous processes, it is a common observation that for endothermic change the entropy change is positive and high. If entropy change is negative then the process is highly exothermic. In selecting Entropy as a criterion of spontaneity, one must consider the entropy changes for both the system and surrounding together ($\Delta S_{\text{universe}}$). But it is always not convenient to do so. Hence it is desirable to use the new functions as criteria of spontaneity which a compromise between ΔE or ΔH and the entropy change of a system without considering the surrounding. These functions are A and G which are a state functions and they are extensive properties of the system.

If the experiment is carried out under conditions of constant volume and temperature we have the function (ΔA) written as;

$$\Delta A = \Delta E - T\Delta S$$

If $\Delta A = 0$ the system the process is at equilibrium (reversible)

$\Delta A > 0$ the process is not spontaneous

$$\Delta A < 0 \text{ the process is spontaneous} \Rightarrow (\Delta s)_{univ} > 0$$

If the experiment is carried out under conditions of constant pressure and temperature, the

$\Delta G = \Delta H - T\Delta S$: If $\Delta G = 0$ the system /the process is at equilibrium

$\Delta G > 0$ the process is not spontaneous

$\Delta G < 0$ the process is spontaneous.

❖ Helmholtz free energy (A)

$$A = E - TS$$

$$dA = dE - TdS - SdT, \text{ But } dE = dq + dW \\ \Rightarrow dA = dq + dW - TdS - SdT$$

For reversible isothermal $dq = TdS$

$$\Rightarrow dA = TdS' + dW - TdS' - SdT$$

$$dA = dW - SdT$$

At constant temperature $dT = 0 \Rightarrow (dA)_T = dW$ or $-(dA) = -dW$

The decrease in Helmholtz free energy is equal to the maximum amount of work which a system can do isothermally. Because of this relation between A and W, A is called as work function.

❖ Gibbs free Energy (G)

It is defined $G = H - TS$ Where $H = E + PV$

$$\Rightarrow G = E + PV - TS$$

$$dG = dE + PdV + VdP - TdS - SdT, \quad \text{Since } dE = TdS + dW_{rev}$$

$$\Rightarrow dG = TdS' + dW_{rev} + PdV + SdT - TdS' - SdT$$

$$(dG)_{PT} = dW_{rev} - (PdV), \text{ here } dW \text{ is all types of work, and } -PdV = \text{mechanical work}$$

$$(dG)_{PT} = dW_{rev} - (-PdV) = W_{net}$$

$$\Rightarrow (dG)_{TP} = W_{net} \Rightarrow -\Delta G = (-W_{net})$$

Thus, the decrease in Gibbs free energy is equal to the amount of maximum work which a system can do isothermally and isobarically over and above the mechanical work. The logic free energy can now be made clear. The difference $\Delta E - T\Delta S$ and $\Delta H - T\Delta S$ are the free energies in the sense that if all the processes are reversible and isothermal than the complete conversion of free energies to work is possible. ΔG or ΔA sometimes called the available work or availability.

• **Relation between A and G**

$$A = E - TS$$

$$G = H - TS, \text{ we know that } H = E + PV$$

$$\Rightarrow G = E + PV - TS = (E - TS) + PV$$

$$G = A + PV$$

For a system changed from G_1 to G_2

$$\Delta G = G_2 - G_1 = (A_2 + P_2V_2) + (A_1 + P_1V_1)$$

$$\Delta G = G_2 - G_1 = (A_2 - A_1) + (P_2V_2 - P_1V_1), PV = nRT$$

$$\Delta G = \Delta A + nR(T_2 - T_1)$$

$$\Delta G = \Delta A + nR\Delta T$$

For an isothermal change $\Delta T = 0 \Rightarrow \Delta G = \Delta A$

$$\Rightarrow \Delta G = \Delta H = -nRT \ln \left[\frac{V_2}{V_1} \right]$$

3.4.3.5. **Gibb's- Helmholtz equation**

Gibb's-Helmholtz equation related the free energy change to the enthalpy change and the rate of change of free energy with temperature.

$$G = H - TS$$

$$H = E + PV \Rightarrow G = E + PV - TS$$

$$dG = dE + PdV + VdP - TdS - SdT$$

By 1st law $dE + PdV = dq$

$$\therefore dG = dq + VdP - TdS - SdT \text{ But for reversible change } dq = TdS$$

$$dG = TdS + VdP - TdS - SdT$$

$$dG = -SdT + VdP$$

For an isobaric change, $dP = 0$ and the above equation yields

$$\left(\frac{\partial G}{\partial T} \right)_P = -S$$

By substitution of $-S$ in to $G = H + T\Delta S$

$$G = H + \left(\frac{\partial G}{\partial T} \right)_P T \Rightarrow G - T \left(\frac{\partial G}{\partial T} \right)_P = H \quad \text{This is Gibbs-Helmholtz equation.}$$

Using Gibbs-Helmholtz equation we can find the rate of change of EMF with temperature in electrochemical cells as follows. For electrical work $\Delta G = -nFE$

$$\Rightarrow -nFE = \Delta H + \left(\frac{\partial(-nFE)}{\partial T} \right)_P T$$

$$-nFE = \Delta H - nFT \left(\frac{\partial E}{\partial T} \right)_P$$

$\left(\frac{\partial E}{\partial T} \right)_P$ is the rate of change of EMF with temperature

Example. For a Daniel cell calculate $\Delta G, \Delta H$ and ΔS using the following data $E = 1.01462 \text{ V}$, at 25°C ,

$$n = 2, F = 96500 \text{ C}, \text{ and } \left(\frac{\partial E}{\partial T} \right)_P = -5.0 \times 10^{-5} \text{ VK}^{-1}$$

Solution

$$\Delta G = -nFE = -195815 \text{ J}$$

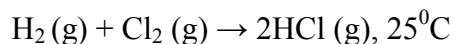
$$\Delta S = - \left(\frac{\partial \Delta G}{\partial T} \right)_P = nF \left(\frac{\partial E}{\partial T} \right)_P = -9.65 \text{ JK}^{-1}$$

$$\Delta H = -nFE + nFT \left(\frac{\partial E}{\partial T} \right)_P = \underline{\underline{-19869 \text{ J}}}$$

Spontaneity and relative values of ΔH and $T\Delta S$

ΔH	ΔS	$\Delta G = \Delta H - T\Delta S$	Conclusion
- (exothermic)	+	At all T	Spontaneous
- (exothermic)	-	- at low T + at high T	Spontaneous Non-spontaneous
+ (endothermic)	+	+ at low T - at high T	Non spontaneous Spontaneous
+ (endothermic)	-	At all T	Forbidden in the forward (non-spontaneous)

Example 3.4.8. calculate the free energy change for the reaction



Given , $\Delta H^\circ (\text{H} - \text{H}) = 435 \text{ KJ/mol}$, $\Delta H^\circ (\text{Cl} - \text{Cl}) = 240 \text{ KJ/mol}$

$$\Delta H^0(H-HCl) = 430 \text{ kJ/mol} \quad S^0(H_2) = 130.59 \text{ J/mol K}$$

$$\Delta S^0(Cl_2) = 22.95 \text{ J/mol K}, S^0(HCl) = 186.68 \text{ J/mol K}$$

Solution $\Delta G^0 = \Delta H^0 - T\Delta S^0$

$$\begin{aligned} \Delta H^0 &= \text{energy absorbed} - \text{energy released} \\ &= \Delta H^0(H-H) + \Delta H^0(Cl-Cl) - 2 \times \Delta H^0(H-Cl) \\ &= (435 + 240 - 2 \times 430) \text{ kJ} = -185 \text{ kJ} \end{aligned}$$

$$\begin{aligned} \Delta S^0 &= \sum S^0_{(\text{products})} - \sum S^0_{(\text{reactants})} \\ &= 2 \times S^0(HCl) - S^0(H_2) - S^0(Cl_2) \\ &= (2 \times 186.68 - 130.59 - 222.95) \text{ J/K} = 19.82 \times 10^{-3} \text{ kJ/K} \end{aligned}$$

$$\begin{aligned} \Delta G &= \Delta H^0 - T\Delta S^0 \\ &= -185 \text{ kJ} - (298 \text{ K}) \times 19.82 \times 10^{-3} \text{ kJ/K} \\ &= \underline{\underline{-190.9 \text{ kJ}}} \quad \Rightarrow \text{Spontaneous or exoergonic} \end{aligned}$$

3.4.4. Maxwell relation

To this point, the state functions U, H, A, and G, all of which have the units of energy have been defined. The functions U and H are used to calculate changes in energy for processes, and A and G are used to calculate the direction in which processes evolve and the maximum work the reactions can produce. In this section, we discuss how these state functions depend on the macroscopic system variables. To do so, the differential forms dU, dH, dA, and dG are developed. As we will see, these differential forms are essential in calculating how U, H, A, and G vary with state variables such as P and T. Starting from the definitions

$$H = U + PV$$

$$A = U - TS$$

$$G = H - TS = U + PV - TS$$

the following total differentials can be formed:

$$dU = TdS - PdV$$

$$dH = TdS - PdV + PdV + VdP = TdS + VdP$$

$$dA = TdS - PdV - TdS - SdT = -SdT - PdV$$

$$dG = TdS + VdP - TdS - SdT = -SdT + VdP$$

These differential forms express the internal energy as $U(S,V)$, the enthalpy as $H(S,P)$, the Helmholtz energy as $A(T,V)$, and the Gibbs energy as $G(T,P)$. Although other combinations of variables can be used, these **natural variables** are used because the differential expressions are compact.

What information can be obtained from the differential expressions in Equations dU through Equations dG? Because U , H , A , and G is state functions, two different equivalent expressions such as those written for dU here can be formulated:

$$dU = TdS - PdV = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

This Equation to be valid, the coefficients of dS and dV on both sides of the equation must be equal.

Applying this reasoning to Equations dU through dG, the following expressions are obtained:

$$\begin{aligned} \left(\frac{\partial U}{\partial S}\right)_V &= T \text{ and } \left(\frac{\partial U}{\partial V}\right)_S = -P & \left(\frac{\partial A}{\partial T}\right)_V &= -S \text{ and } \left(\frac{\partial A}{\partial V}\right)_T = -P \\ \left(\frac{\partial H}{\partial S}\right)_P &= T \text{ and } \left(\frac{\partial H}{\partial P}\right)_S = V & \left(\frac{\partial G}{\partial T}\right)_P &= -S \text{ and } \left(\frac{\partial G}{\partial P}\right)_T = V \end{aligned}$$

These expressions state how U , H , A , and G vary with their natural variables. For example, because T and V always have positive values, Equation H above states that H increases if either the entropy or the pressure of the system increases. There is also a second way in which the differential expressions in Equations dU through dG can be used. We know that because dU is an exact differential:

$$\left(\frac{\partial}{\partial V} \left(\frac{\partial U(S,V)}{\partial S}\right)_V\right)_S = \left(\frac{\partial}{\partial S} \left(\frac{\partial U(S,V)}{\partial V}\right)_S\right)_V$$

The relations derived from the fundamental these equations, based on the criteria of exact differential (state function in physical chemistry) are called **Maxwell's Relation**.

$$\begin{aligned} dU &= TdS - PdV \Rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \\ dH &= TdS + VdP \Rightarrow \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \\ dA &= -SdT - PdV \Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \\ dG &= -SdT + VdP \Rightarrow -\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \end{aligned}$$

Example 3.6

Show that $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$

Solution

Because U is a state function, $\left(\frac{\partial}{\partial V}\left(\frac{\partial U(S,V)}{\partial S}\right)\right)_S = \left(\frac{\partial}{\partial S}\left(\frac{\partial U(S,V)}{\partial V}\right)\right)_V$.

Substituting $dU = TdS - PdV$ in the previous expression,

$$\left(\frac{\partial}{\partial V}\left(\frac{\partial[TdS - PdV]}{\partial S}\right)\right)_S = \left(\frac{\partial}{\partial S}\left(\frac{\partial[TdS - PdV]}{\partial V}\right)\right)_V$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

3.5. The third law of thermodynamics

The variation of entropy of a substance with temperature at constant pressure is given by

$$dS = \frac{C_P}{T} dT$$

$$\int_{T_1}^{T_2} dS = S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{C_P}{T} dT$$

$$\Rightarrow S(T_2) = S(T_1) + \int_{T_1}^{T_2} \frac{C_P}{T} dT$$

$\Rightarrow S(T_2)$ can be evaluated provided the quantities on the right hand side of this equation are known. C_P can be measured experimentally over a range of temperature but the problem remains to find the value of $S(T_1)$. This problem is solved by assigning a zero value to $S(T_1)$ at absolute zero as stated below by the third law of thermodynamics.

Statement of third law of thermodynamics:

“Every substance has finite positive entropy, but at absolute zero (0K) the entropy may become zero and does so in case of a perfectly crystalline substance.”

The statement is confined to pure crystalline solids because theoretical arguments and evidence have shown that the entropy of solutions and super cooled liquids is not zero. For pure crystalline solids the law has been varied repeatedly.

Thus as $T \rightarrow 0$, $S(T) \rightarrow 0$

$$\Rightarrow S^0(T) = \int_0^T \frac{C_P}{T} dT$$

Where $S^0(T)$ is the absolute entropy of a substance at a temperature T K and it is appositve quantity. Its value can be calculated if we integrate the right hand side of the equation (4.45) from $T=0$ to any desired temperature T . To be able to integrate we must know the value of right from $T=0$ to the desired temperature T .