

## Second Law of Thermodynamics

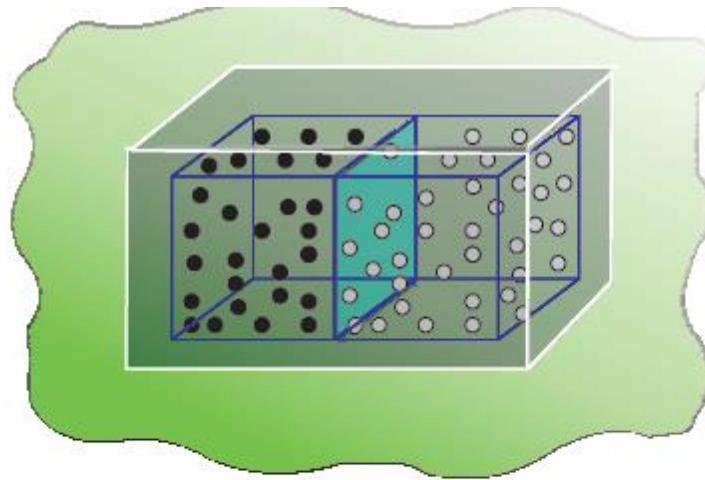
### Spontaneity

The first law of thermodynamics tells us about the relationship between the heat absorbed and the work performed on or by a system. It puts no restrictions on the direction of heat flow. However, the flow of heat is unidirectional from higher temperature to lower temperature. In fact, all naturally occurring processes whether chemical or physical will tend to proceed spontaneously in one direction only. For example, a gas expanding to fill the available volume, burning carbon in dioxygen giving carbon dioxide.

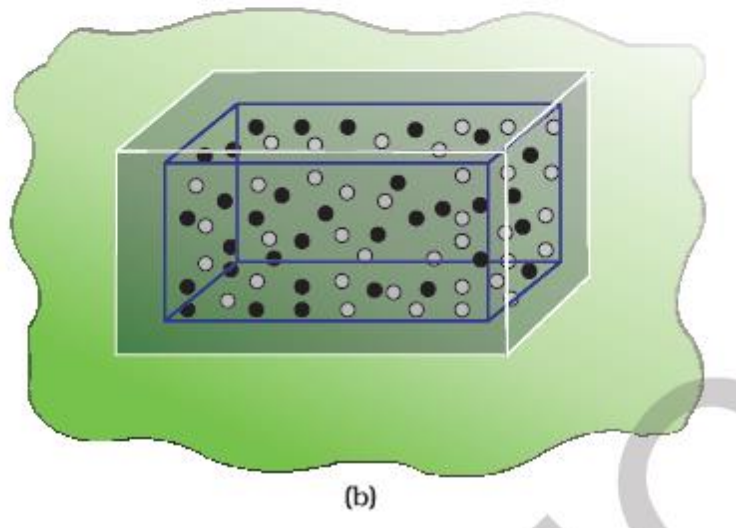
But heat will not flow from colder body to warmer body on its own, the gas in a container will not spontaneously contract into one corner or carbon dioxide will not form carbon and dioxygen spontaneously. These and many other spontaneously occurring changes show unidirectional change. We may ask 'what is the driving force of spontaneously occurring changes ? What determines the direction of a spontaneous change ? In this section, we shall establish some criterion for these processes whether these will take place or not.

Let us first understand what do we mean by spontaneous reaction or change ? You may think by your common observation that spontaneous reaction is one which occurs immediately when contact is made between the reactants. Take the case of combination of hydrogen and oxygen. These gases may be mixed at room temperature and left for many years without observing any perceptible change. Although the reaction is taking place between them, it is at an extremely slow rate. It is still called spontaneous reaction. So spontaneity means '*having the potential to proceed without the assistance of external agency*'. However, it does not tell about the rate of the reaction or process. Another aspect of spontaneous reaction or process, as we see is that these cannot reverse their direction on their own. A spontaneous process is an irreversible process and may only be reversed by some external agency. It is found that many of the exothermic and endothermic reactions are spontaneous and so decreasing  $\Delta H$  cannot be considered as the criteria for the spontaneity. Then, what drives the spontaneous process in a given direction ? Let us examine such a case in which  $\Delta H = 0$  i.e., there is no change in enthalpy, but still the process is spontaneous.

Let us consider diffusion of two gases into each other in a closed container which is isolated from the surroundings as shown in figure.



(a)



(b)

The two gases, say, gas A and gas B are represented by black dots and white dots respectively and separated by a movable partition [Fig.(a)]. When the partition is withdrawn [Fig.( b)], the gases begin to diffuse into each other and after a period of time, diffusion will be complete. Let us examine the process. Before partition, if we were to pick up the gas molecules from left container, we would be sure that these will be molecules of gas A and similarly if we were to pick up the gas molecules from right container, we would be sure that these will be molecules of gas B. But, if we were to pick up molecules from container when partition is removed, we are not sure whether the molecules picked are of gas A or gas B. We say that the system has become less predictable or more chaotic. We may now formulate another postulate: in an isolated system, there is always a tendency for the systems' energy to become more disordered or chaotic and this could be a criterion for spontaneous change !.

At this point, we introduce another thermodynamic function, entropy denoted as  $S$ . The above mentioned disorder is the manifestation of entropy. To form a mental picture, one can think of entropy as a measure of the degree of randomness or disorder in the system. The greater the disorder in an isolated system, the higher is the entropy. Entropy, like any other thermodynamic property such as internal energy  $U$  and enthalpy  $H$  is a state function and  $\Delta S$  is independent of path. Whenever heat is added to the system, it increases molecular motions causing increased randomness in the system. Thus heat ( $q$ ) has randomising influence on the system.

A system at higher temperature has greater randomness in it than one at lower temperature. Thus, temperature is the measure of average chaotic motion of particles in the system. Heat added to a system at lower temperature causes greater randomness than when the same quantity of heat is added to it at higher temperature. This suggests that the entropy change is inversely proportional to the temperature.  $\Delta S$  is related with  $q$  and  $T$  for a reversible reaction as :

$$\Delta S = \frac{q_{rev}}{T} \quad (1)$$

The total entropy change ( $\Delta S_{total}$ ) for the system and surroundings of a spontaneous process is given by

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surr} > 0 \quad (2)$$

When a system is in equilibrium, the entropy is maximum, and the change in entropy,  $\Delta S = 0$ . We can say that entropy for a spontaneous process increases till it reaches maximum and at equilibrium the change in entropy is zero. Since entropy is a state property, we can calculate the change in entropy of a reversible process by

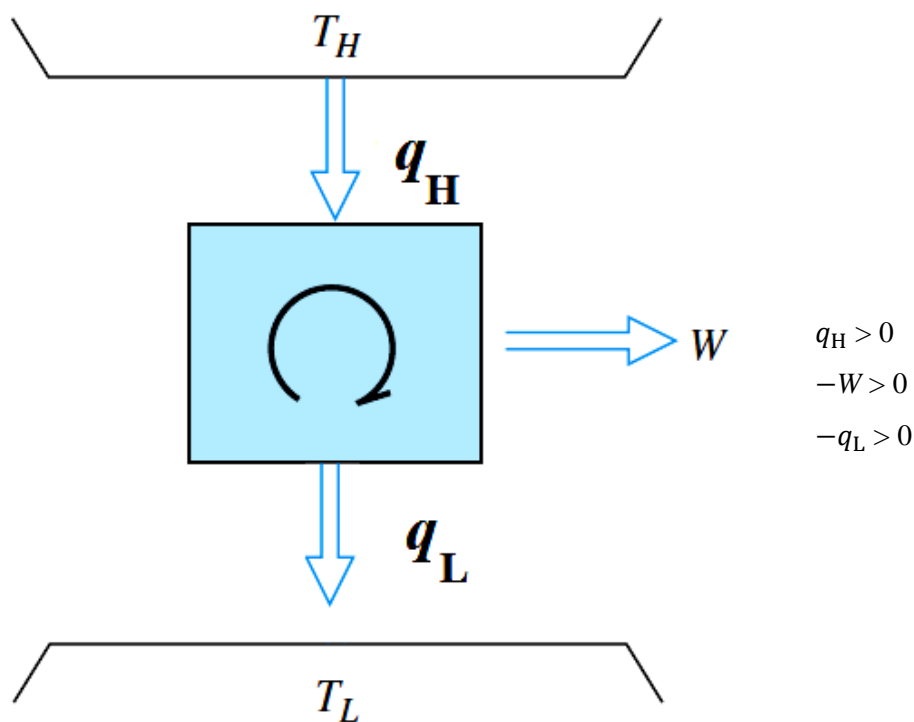
$$\Delta S_{total} = \frac{q_{system, rev}}{T} \quad (3)$$

We find that both for reversible and irreversible expansion for an ideal gas, under isothermal conditions,  $\Delta U = 0$ , but  $\Delta S_{total}$  i.e.  $\Delta S_{system} + \Delta S_{surr}$  is not zero for irreversible process. Thus  $\Delta U$  does not discriminate reversible and irreversible process whereas  $\Delta S$  does.

## Statements of Second law of thermodynamics

### The Kelvin-Planck Statement

*“It is impossible to construct a device that will operate in a cycle and produce no effect other than the raising of a weight and the exchange of heat with a single reservoir.”* This statement is related to the heat engine. In effect it states that it is impossible to construct a heat engine that operate in a cycle, receives a given amount of heat from high temperature body and does an equal amount of work. The only alternative is that some heat must be transferred to a low temperature body. Thus work can be done by the transfer of heat only if there are two temperature levels and heat is transferred from the high temperature body to the heat engine and also from the heat engine to the low temperature body. This implies that it is impossible to build a heat engine that has a thermal efficiency of 100 %.



$T_H$  = High temperature body

$T_L$  = Low temperature body

Let  $q_H$  be the heat entered to the system which run in a cycle.  $W$  is the work done by the system.  $q_L$  be the heat transferred from the system to the low temperature body.

From the first law of thermodynamics and for a cyclic process  $\Delta U = 0$ .

$$W + q_H + q_L = 0$$

$$-W = q_H + q_L$$

$$\text{Efficiency} = \frac{\text{Work out}}{\text{Heat in}} = \frac{-W}{q_H}$$

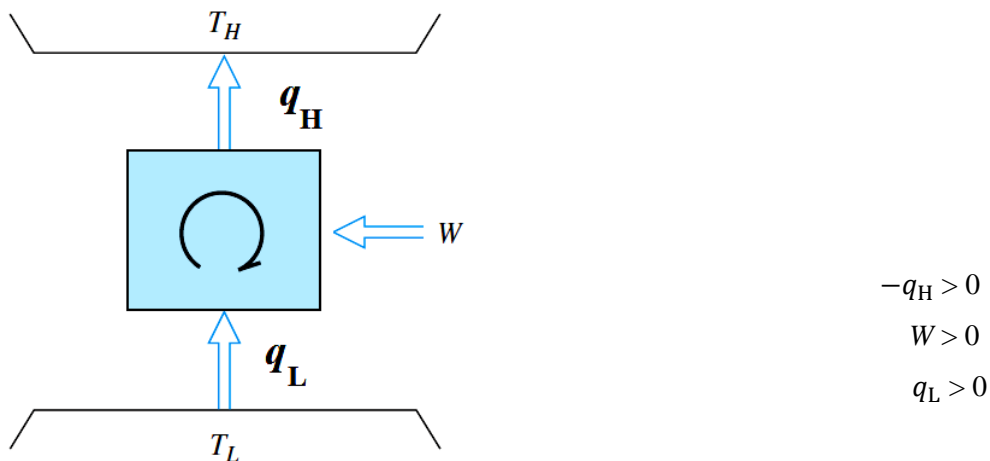
$$= \frac{q_H + q_L}{q_H}$$

$$= 1 + \frac{q_L}{q_H}$$

Here efficiency is always less than one because  $q_L < 0$ .

### The Clausius statement

“It is impossible to construct a device that operate in a cycle and produce no effect other than the transfer of heat from a cooler body to a warmer body.” This statement is related to the refrigerator or heat pump. In effect, it is impossible to construct a refrigerator without an input of work.



Let  $q_L$  be the heat entered to the system which run in a cycle.  $W$  is the work done on the system.  $q_H$  be the heat transferred to the high temperature body from the system. By the first law of thermodynamics

$$W + q_H + q_L = 0$$

$$W + q_L = -q_H$$

## The Carnot Cycle

In 1824 a French engineer, Sadi Carnot, investigated the principles governing the transformation of thermal energy, "heat," into mechanical energy, work. He based his discussion on a cyclical transformation of a system that is now called the Carnot cycle. The Carnot cycle consists of four reversible steps, and therefore is a reversible cycle. A system is subjected consecutively to the reversible changes in state:

Step 1 . Reversible isothermal expansion.

Step 3. Reversible isothermal compression.

Step 2. Reversible adiabatic expansion.

Step 4. Reversible adiabatic compression.

Since the mass of the system is fixed, the state can be described by any two of the three variables  $T$ ,  $p$ ,  $V$ . A system of this sort that produces only heat and work effects in the surroundings is called a heat engine. A heat reservoir is a system that has the same temperature everywhere within it; this temperature is unaffected by the transfer of any desired quantity of heat into or out of the reservoir.

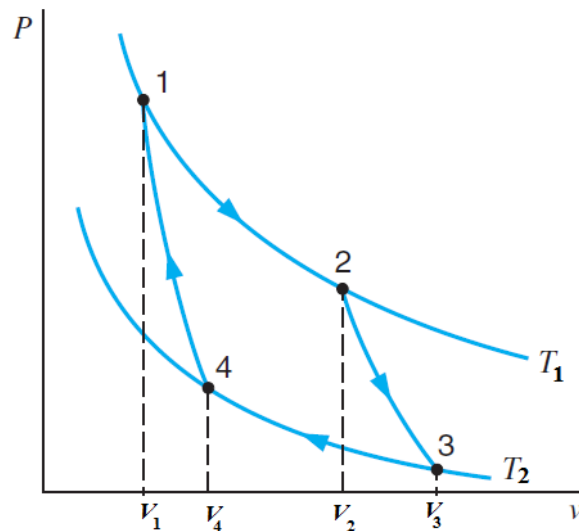


Figure 1

- |       |                                   |
|-------|-----------------------------------|
| 1 → 2 | Reversible isothermal expansion   |
| 2 → 3 | Reversible adiabatic expansion    |
| 3 → 4 | Reversible isothermal compression |
| 4 → 1 | Reversible adiabatic compression  |

Dr. Biju A R

$$\text{Efficiency of the heat engine, } \epsilon = \frac{\text{Work out}}{\text{Heat in}} = \frac{W}{Q}$$

$$\text{Total work out } W = -(W_1 + W_1' + W_2 + W_2')$$

$$\text{Heat input } Q = q_1$$

$$\epsilon = \frac{-(W_1 + W_1' + W_2 + W_2')}{q_1}$$

$$\text{For a cyclic process } \oint dU = 0$$

From the first law of thermodynamics

$$q_1 + q_2 = -(W_1 + W_1' + W_2 + W_2')$$

$$\text{So } \epsilon = \frac{q_1 + q_2}{q_1} = 1 + \frac{q_2}{q_1}$$

Since  $q_2$  is the heat flowed out from the system and it is negative ;  $\epsilon$  is always less than one.

### Step 1 . Reversible Isothermal expansion.

In Step 1, the cylinder is immersed in a heat reservoir at a temperature  $T_1$  and is expanded isothermally from the initial volume  $V_1$  to a volume  $V_2$ . During this expansion step, the piston does work  $|W_1|$  on the surroundings, and heat is absorbed by the gas from the high-temperature reservoir. Note that according to the convention that  $W_1$  is negative.

$$\text{For isothermal expansion } \Delta U = q_1 + W_1$$

$$\text{For isothermal expansion of ideal gases, } \Delta U = 0$$

$$0 = q_1 + W_1$$

$$q_1 = -W_1$$

$$q_1 = \int_1^2 p dV$$

$$q_1 = RT_1 \ln\left(\frac{V_2}{V_1}\right)$$

### Step 2. Reversible Adiabatic expansion.

The cylinder is now taken out of the reservoir, insulated; and in Step 2 is expanded adiabatically from  $V_2$  to  $V_3$ ; in this step the temperature of the system drops from  $T_1$  to a

lower temperature  $T_2$ . For this step we assume that the piston and cylinder are thermally insulated so that no heat is gained or lost. The expansion continues until the temperature of the gas has dropped to  $T_2$ . During this expansion step, the piston does work  $|W'_1|$  on the surroundings.

$$\text{Adiabatic expansion } \Delta U_2 = W'_1$$

$$\Delta U_2 = C_v (T_2 - T_1), \frac{T_2}{T_1} = \left(\frac{V_2}{V_3}\right)^{\gamma-1}$$

### Step 3. Reversible Isothermal compression.

The insulation is removed and the cylinder is placed in a heat reservoir at  $T_2$ . In Step 3 the system is compressed isothermally from  $V_3$  to  $V_4$ . The cylinder is removed from the reservoir and insulated again. During this compression step the surroundings do work  $|W_2|$  on the gas, and heat flows out of the gas to the low-temperature heat reservoir. Note that according to the convention that  $q_2$  is the heat given by the gas,  $q_2$  is negative.

$$\text{Reversible isothermal compression } \Delta U_3 = q_2 + W_2$$

$$\text{For isothermal expansion of ideal gases, } \Delta U = 0$$

$$q_2 = -W_2$$

$$= RT_2 \ln\left(\frac{V_4}{V_3}\right)$$

### Step 4. Reversible adiabatic compression

In Step 4 the system is compressed adiabatically from  $V_3$  to  $V_4$  the original volume. In this adiabatic compression, the temperature rises from  $T_2$  to  $T_1$  the original temperature. Thus, as it must be in a cycle, the system is restored to its initial state. This step completes the cycle by bringing the gas back to its initial state at temperature. During this compression step, the surroundings do work on the gas, but no heat is gained or lost.

$$\text{Reversible adiabatic compression } \Delta U_4 = W'_2, = C_v (T_1 - T_2); \frac{T_1}{T_2} = \left(\frac{V_4}{V_1}\right)^{\gamma-1}$$

$$\frac{T_2}{T_1} = \left(\frac{V_2}{V_3}\right)^{\gamma-1} \text{ and } ; \frac{T_1}{T_2} = \left(\frac{V_4}{V_1}\right)^{\gamma-1} \text{ an inverse relation so } \frac{V_2}{V_3} = \frac{V_1}{V_4}; \frac{V_4}{V_3} = \frac{V_1}{V_2}$$

$$\epsilon = 1 + \frac{q_2}{q_1}$$



$$\begin{aligned}
 &= 1 + \frac{RT_2 \ln\left(\frac{V_4}{V_3}\right)}{RT_1 \ln\left(\frac{V_2}{V_1}\right)} \\
 &= 1 + \frac{RT_2 \ln\left(\frac{V_1}{V_2}\right)}{RT_1 \ln\left(\frac{V_2}{V_1}\right)} \\
 &= 1 - \frac{RT_2 \ln\left(\frac{V_2}{V_1}\right)}{RT_1 \ln\left(\frac{V_2}{V_1}\right)} \\
 \epsilon &= 1 - \frac{T_2}{T_1}
 \end{aligned}$$

So the efficiency of the heat engine is always less than one. We know that high efficiency can be obtained by keeping the ratio  $\frac{T_2}{T_1}$  a lower value as much as possible and efficiency is 100 % when the low temperature reservoir  $T_2$  is at 0 K.

Since

$$\begin{aligned}
 \epsilon &= 1 + \frac{q_2}{q_1} \\
 \epsilon &= 1 - \frac{T_2}{T_1} \\
 1 + \frac{q_2}{q_1} &= 1 - \frac{T_2}{T_1} \\
 \frac{q_2}{q_1} &= -\frac{T_2}{T_1} \\
 \frac{q_2}{T_2} + \frac{q_1}{T_1} &= 0
 \end{aligned}$$

Therefore any closed system undergoing a Carnot cycle

$$\oint \frac{dq_{rev}}{T} = \frac{q_2}{T_2} + \frac{q_1}{T_1} = 0$$

The subscript rev reminds us that the cycle under consideration is reversible. Since the integral of  $\frac{dq_{rev}}{T}$  any reversible cycle is zero, it follows that the value of line integral  $\int_1^2 \frac{dq_{rev}}{T}$  is independent of the path between the states 1 and 2 and depends only on the initial and final states. Hence  $\frac{dq_{rev}}{T}$  is the differential of a state function. This state function is called the entropy S.

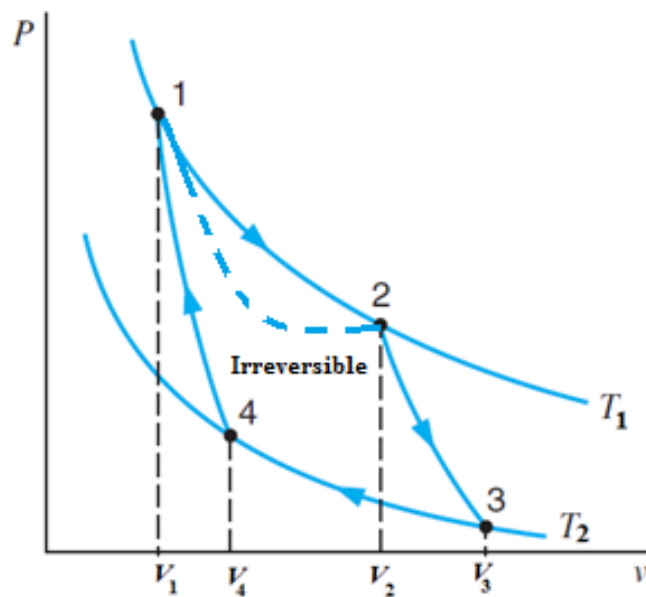
$$dS = \frac{dq_{rev}}{T} \text{ for reversible process.}$$

The entropy change going from state 1 to state 2 equals

$$\Delta S = S_2 - S_1 = \int_1^2 \frac{\delta q_{rev}}{T}$$

If a system goes from state 1 to state 2 by an irreversible process, intermediate state it pass through may not be states of equilibrium and the entropies temperatures etc of intermediate states may be undefined. However since S is a state function it doesn't matter how the system went from state 1 to 2 ;  $\Delta S$  is same for any process that connects states 1 and 2. But it is only for reversible process that the integral of  $\frac{\delta q_{rev}}{T}$  gives the entropy changes. Calculation of  $\Delta S$  in an irreversible process is considered in the next section. Clausius discovered the state function S in 1854 and called the transformation content. Later he renamed it entropy, from Greek word trop means transformation, since S is related to the transformation of heat to work.

Now consider another Carnot cycle with an irreversible step as shown below.



From 1 → 2 Expansion work from 1 to 2,  $(-W)_{irreversible} < (-W)_{reversible}$

$(W)_{irreversible} > (W)_{reversible}$

Since internal energy is a state function, it depends only on the initial and final state.

$$\Delta U = q_{irrev} + W_{irrev}$$

$$\Delta U = q_{rev} + W_{rev}$$

$$\text{So } q_{rev} > q_{irrev}$$

$$\epsilon = 1 + \frac{q_2^{rev}}{q_1^{irrev}} < 1 + \frac{q_2^{rev}}{q_1^{rev}}$$

$$\frac{\dot{q}_{irrev}}{T} < \frac{\dot{q}_{rev}}{T} = \oint \frac{\dot{q}_{irrev}}{T} < \oint \frac{\dot{q}_{rev}}{T}$$

$$\oint \frac{\dot{q}_{irrev}}{T} < 0$$

$$\oint \frac{\dot{q}_{rev}}{T} = 0$$

$$\oint \frac{\dot{q}}{T} \leq 0$$

The above expression is called **Clausius inequality**.

### Reversible process

In a reversible process the heat  $q_{rev}$  taken up by the system is supplied in a reversible manner by a heat reservoir (surroundings). Suppose all of the procedures taking place at T K.

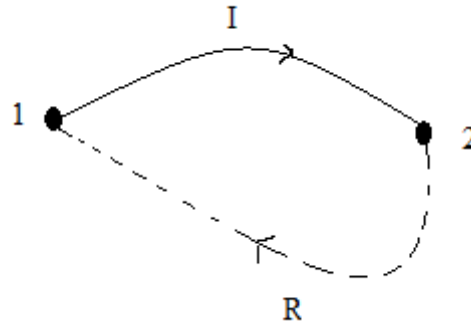
$$\text{Entropy change of system } \Delta S_{\text{system}} = \frac{\dot{q}_{rev}}{T}$$

$$\text{Entropy changes of surroundings } \Delta S_{\text{surroundings}} = - \frac{\dot{q}_{rev}}{T}$$

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

$$= \frac{\dot{q}_{rev}}{T} - \frac{\dot{q}_{rev}}{T} = 0$$

**Irreversible process**



We start with 1 and proceed to 2 along I which represents irreversible process. We return from 2 to 1 along path R which represents reversible process. From Clausius inequality we know that

$$0 \geq \oint \frac{\delta q}{T}$$

$$\oint \frac{\delta q}{T} = \int_1^2 \frac{\delta q_{irre}}{T} + \int_2^1 \frac{\delta q_{rev}}{T}$$

$$0 \geq \int_1^2 \frac{\delta q_{irre}}{T} + \int_2^1 \frac{\delta q_{rev}}{T}$$

$$0 \geq \int_1^2 \frac{\delta q_{irre}}{T} + \int_2^1 dS$$

Since the second process is reversible limits can be interchanged

$$0 \geq \int_1^2 \frac{\delta q_{irre}}{T} - \int_1^2 dS$$

On rearranging we have

$$\int_1^2 dS \geq \int_1^2 \frac{\delta q_{irre}}{T}$$

If the changes from state 1 to 2 is an infinitesimal one

$$dS \geq \int_1^2 \frac{\delta q_{irre}}{T}$$

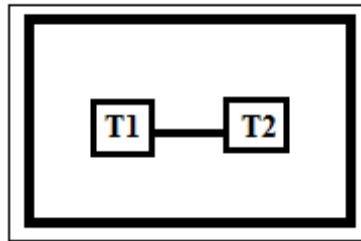
This is another form of Clausius inequality which is a fundamental requirement for a real transformations. We will not ordinarily use the above equation just as it stands but will manipulate it to express the inequality in term of state function of a system, rather than in terms of a path property such as  $\delta q_{irre}$

The Clausius inequality can be applied to changes in an isolated system. The entire universe can be considered as an isolated system. The Clausius inequality can be applied to changes in an isolated system. For any change in the state in an isolated system  $\oint \delta q_{irre} = 0$ . The inequality then becomes

$$dS \geq 0$$

The requirement for real transformations in an isolated system is that  $dS$  must be positive; the entropy must increase. The entropy of an isolated system continues to increase so long as changes occur within it. When the changes cease, the system is in equilibrium and the entropy has reached a maximum value. Therefore the condition of equilibrium in an isolated system is that the entropy have a maximum value. These, then, are also fundamental properties of the entropy : (1) the entropy of an isolated system is increased by any natural change which occurs within it ; and (2) the entropy of an isolated system has a maximum value at equilibrium.

### Heat flow



Consider an isolated system. Total internal energy change for an isolated system is zero.  $\Delta U = 0$ . Suppose  $T_2$  is a hotter body and heat flows naturally from  $T_2$  to  $T_1$ .

$$dS = dS_1 + dS_2$$

$$dS = \frac{\delta q_1}{T_1} + \frac{\delta q_2}{T_2}$$

$$\delta q_1 = -\delta q_2 \quad \text{or} \quad \delta q_2 = -\delta q_1$$

$$dS = \delta q_1 \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$dS = \delta q_1 \left( \frac{T_2 - T_1}{T_2 T_1} \right)$$

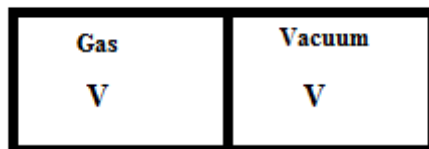
We know that  $dS > 0$  for spontaneous change to occur. Since  $T_2$  is hotter  $\delta q_1$  is positive.

Dr. Biju A R

If  $T_1 > T_2$ ,  $\left(\frac{T_2 - T_1}{T_2 T_1}\right)$  is negative so  $\delta q_1$  should be negative to have  $dS$  a positive value. Ie

Heat must flow from  $T_1$  to  $T_2$ .

### Joules Expansion of ideal gas



$$1 \text{ mol (g, } V, T) = 1 \text{ mol (g, } 2V, T)$$

Consider one mole of an ideal gas occupy volume  $V$  in a compartment. The other compartment with volume  $V$  is partitioned and kept in vacuum. The entire system is isolated and so on removal of the partition gas expands adiabatically. On removal of the partition gases expands adiabatically into a total volume of  $2V$ . The entire process is an irreversible process. Since it is an isolated system  $\Delta U$  is zero.

$$\begin{aligned}\Delta S_{back} &= \int \frac{\delta q_{rev}}{T} = \int \frac{-dW}{T} \\ &= \int_{2V}^V \frac{p dV}{T} \\ &= R \int_{2V}^V \frac{dV}{V} \\ &= R \ln \frac{V}{2V} \\ &= R \ln \frac{1}{2}\end{aligned}$$

$$\Delta S_{forward} = R \ln 2$$

It is a positive number and the forward process is spontaneous.

**(1) Variation of entropy with temperature**

**(a) At constant Volume.**

From first law of thermodynamics

$$dU = \delta q - pdV$$

$$dU + pdV = \delta q$$

By dividing both sides by T

$$\frac{dU + pdV}{T} = \frac{\delta q}{T}$$

$$\frac{c_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV + pdV}{T} = dS$$

$$\frac{c_v dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]dV}{T} = dS \quad (1)$$

Suppose entropy is the function of T and V, S(T, V)

$$\left(\frac{\partial s}{\partial T}\right)_V dT + \left(\frac{\partial s}{\partial V}\right)_T dV = dS \quad (2)$$

By comparing equation 1 and 2, we will get

$$\left(\frac{\partial s}{\partial T}\right)_V = \frac{c_v}{T}$$

$$\left(\frac{\partial s}{\partial V}\right)_T = \frac{\left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]dV}{T}$$

At constant volume  $\left(\frac{\partial s}{\partial V}\right)_T$  is equal to zero since  $dV$  is equal to zero. So  $dS$  will be equal to

$$dS = \frac{1}{T} [C_v dT]$$

For an infinitesimal change

$$\Delta S = S_2 - S_1 = C_v \int_{T_1}^{T_2} \frac{dT}{T}$$

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

$$\Delta S = 2.303 C_v \log \left( \frac{T_2}{T_1} \right) \text{ at constant volume.}$$

**(b) At constant pressure**

S( T, P)

$$dS = \left( \frac{\partial s}{\partial T} \right)_p dT + \left( \frac{\partial s}{\partial P} \right)_T dp \quad (3)$$

$$U = H - pV$$

$$dU = dH - pdV - VdP \quad (4)$$

From first law of thermodynamics we know that

$$\delta q = dU + pdV \quad (5)$$

Combining equation 4 and 5, we will get

$$\delta q = dH - pdV - VdP + pdV$$

$$\delta q = dH - VdP \quad (6)$$

Dividing equation 6 by T, we will get

$$\frac{\delta q}{T} = \frac{dH}{T} - \frac{Vdp}{T}$$

$$dS = \frac{1}{T} [dH - Vdp] \quad (7)$$

Suppose H ( T, p)

$$dH = \left( \frac{\partial H}{\partial T} \right)_p dT + \left( \frac{\partial H}{\partial P} \right)_T dp \quad (8)$$

$$dS = \frac{1}{T} \left[ \left( \frac{\partial H}{\partial T} \right)_p dT + \left( \frac{\partial H}{\partial P} \right)_T dp - Vdp \right]$$

$$dS = \frac{1}{T} \left( \frac{\partial H}{\partial T} \right)_p dT + \left[ \left( \frac{\partial H}{\partial P} \right)_T - V \right] dp$$

At constant pressure  $dp = 0$



$$dS = \frac{1}{T} \left( \frac{\partial H}{\partial T} \right)_p dT$$

$$\left( \frac{dS}{dT} \right)_p = \frac{1}{T} C_p$$

Substituting the value for  $\left( \frac{dS}{dT} \right)_p$  in equation 3

$$dS = \frac{1}{T} C_p dT + \left( \frac{\partial S}{\partial P} \right)_T dp$$

At constant pressure  $dp$  is zero

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

For an infinitesimal change

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

$\Delta S = 2.303 C_p \log \left( \frac{T_2}{T_1} \right)$	, at constant
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Pressure

## (2) Entropy changes in isothermal expansion of an ideal gas

In isothermal expansion of an ideal gas carried out reversibly, there will be no change in internal energy ie  $\Delta U = 0$  and hence from the first law  $\Delta U = q + w$ ,  $q_{rev} = -w$ . In such a case, the work done in the expansion of  $n$  moles of a gas from volume  $V_1$  to  $V_2$  at constant temperature  $T$  is given by

$$-w = nRT \ln \left( \frac{V_2}{V_1} \right)$$

$$q_{rev} = -w = nRT \ln \left( \frac{V_2}{V_1} \right)$$

$$\Delta S = \frac{q_{rev}}{T}$$

$\Delta S = nR \ln \left( \frac{V_2}{V_1} \right)$
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### (3) Calculation of entropy change of an ideal gas with p, V and T

Since entropy of a system varies with the state of the system, its value for a pure gaseous substance will depend upon any two of the three variables T, p and V. Since T is taken generally as one of the variables, the second variable to be considered may be V and p, thus two variables to be considered are either T and V or T and p.

#### (a) When T and V are the two variables

The increase in entropy the gas for infinitesimally small changes is given by the expression

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

Where  $dq_{rev}$  is the small amount of heat absorbed by the system reversibly from the surroundings at a temperature T.

According to the equation of the first law of the thermodynamics  $\Delta U = q + w$ , we have

$$\delta q_{rev} = dU - \delta w$$

If work involved is due to expansion of the gas, for an infinitesimal increase in volume  $dV$  against a pressure P.

$$-\delta w = pdV \text{ and } dU = C_v dT$$

$$dq_{rev} = C_v dT + pdV$$

For one mole of an ideal gas

$$\delta q_{rev} = C_v dT + RT \frac{dV}{V}$$

$$\frac{\delta q_{rev}}{T} = C_v \frac{dT}{T} + R \frac{dV}{V}$$

For a finite change of state of a system, the entropy changes  $\Delta S$  is obtained by integrating the above equation between the limits of the initial state 1 and the final state 2. Assuming  $C_v$  to be constant within the temperature range  $T_1$  and  $T_2$ , for one mole of the gas we have

$$\Delta S = S_2 - S_1 = C_v \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{V_1}^{V_2} \frac{dV}{V}$$

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

Thus for n moles of the ideal gases, the above equation may be written as

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

It is evident that the entropy change for the change of state of an ideal gas depends upon the initial and final volumes as well as on the initial and final temperatures.

#### (b) When T and p are the two variables

If  $p_1$  is the pressure of the ideal gas in the initial state and  $p_2$  in the final state, then

$p_1 V_1 = RT_1$  and  $p_2 V_2 = RT_2$  for one mole of an ideal gas at initial and final state

$$\frac{V_2}{V_1} = \frac{p_1 T_2}{p_2 T_1}$$

Substituting in the above equation for  $\Delta S$

$$\Delta S = C_V \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{p_2}{p_1}\right)$$

Remembering  $C_V + R = C_p$

$$\Delta S = C_p \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{p_2}{p_1}\right)$$

For n moles of the ideal gas

$$\Delta S = nC_p \ln\left(\frac{T_2}{T_1}\right) - nR \ln\left(\frac{p_2}{p_1}\right)$$

It is evident from the above equations that the entropy change of state of an ideal gas depends on the initial and final pressure as well as on the initial and final temperature.

#### (4) Entropy change during phase transitions

The entropy of a substance changes when a substance freezes or boils as a result of changes in the orderliness with which the molecules pack together and the extent to which the energy is localized or dispersed. For example, when a substance vaporizes, a compact condensed

phase changes into a widely dispersed gas and we can expect the entropy of the substance to increase considerably. The entropy of a solid also increases when it melts to a liquid and when that liquid turns into a gas. Although we can understand the changes of entropy in these statistical, molecular terms, it is far easier to use classical thermodynamics to calculate numerical values, and we shall do that here.

Consider a system and its surroundings at the normal transition temperature,  $T_{\text{trs}}$ , the temperature at which two phases are in equilibrium at 1 atm. This temperature is  $0^{\circ}\text{C}$  (273 K) for ice in equilibrium with liquid water at 1 atm, and  $100^{\circ}\text{C}$  (373 K) for water in equilibrium with its vapour at 1 atm. At the transition temperature, any transfer of energy as heat between the system and its surroundings is reversible because the two phases in the system are in equilibrium. Because at constant pressure  $q = \Delta_{\text{trs}}H$ , the change in molar entropy of the system is

$$\Delta_{\text{trs}}S = \frac{\Delta_{\text{trs}}H}{T}$$

$\Delta_{\text{trs}}H$  is an enthalpy change per mole of substance; so  $\Delta_{\text{trs}}S$  is also a molar quantity with units joules per kelvin per mole ( $\text{J K}^{-1} \text{mol}^{-1}$ ). If the phase transition is exothermic ( $\Delta_{\text{trs}}H < 0$ , as in freezing or condensing), then the entropy change is negative. This decrease in entropy is consistent with localization of matter and energy that accompanies the formation of a solid from a liquid or a liquid from a gas. If the transition is endothermic ( $\Delta_{\text{trs}}H > 0$ , as in melting and vaporization), then the entropy change is positive, which is consistent with dispersal of energy and matter in the system.

### Standard Entropy

Entropy of one mole of a substance in pure state at one atm pressure and  $25^{\circ}\text{C}$  is termed as standard entropy of that substance and is denoted as  $S^0$ . When a reaction involves each reactant and each product in its standard state, the entropy change is said to be standard entropy change. This is denoted by  $\Delta S^0$ . The general equation is then written as

$$\Delta S^0 = \sum S_{\text{products}}^0 - \sum S_{\text{reactants}}^0$$

Entropies of various substances at any given temperature and pressure can be calculated by applying third law of thermodynamics. Standard entropies of some of the important substances obtained in this manner are given below

Substance	Absolute entropy JK <sup>-1</sup> mol <sup>-1</sup>
Hydrogen (g)	130.60
Oxygen (g)	205.01
Water (l)	70.29
Water (g)	188.74

### Physical significance of Entropy

**1. Entropy as a measure of the Disorder of the system.** It has already been shown that all spontaneous process, such as flow of heat from a hot end to a cold end of the conductor, flow of electricity from a point of a higher potential to a point of a lower potential, expansion of a gas in vacuum, diffusion of a solute from concentrated to a dilute solution are accompanied by increase in entropy as well as the disorder of the system.

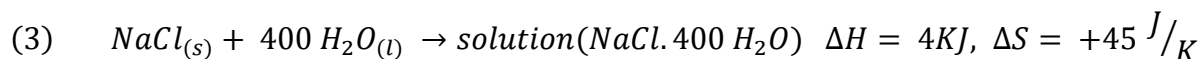
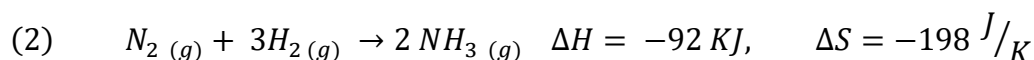
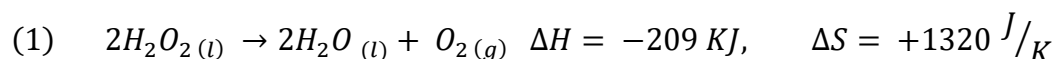
It has also been shown that melting of a solid or evaporation of liquid is accompanied by increase in entropy. At the same time, it is known that the solid has a definite crystal lattice ie the atoms or ions or molecules in a solid are arranged in a definite order. The order is much less in a liquid and least in a gas. Thus increase of entropy implies increase in disorder. Thus entropy is regarded as a measure of the disorder of the system.

**2. Entropy as a measure of probability.** As seen above, all spontaneous process lead to increase in entropy and also to increase in disorder. A little consideration will show that when a process is spontaneous it means that it is proceeding from a less probable to more probable state. It appears, therefore that there is close relation between entropy  $S$  and the thermodynamic probability  $W$  of the state of the system both of which increase at the same time. This relationship was expressed by Boltzmann as

$$S = k \ln W + \text{constant}$$

Where  $k$  is Boltzmann constant ie gas constant per single molecule  $\left(\frac{R}{N_A}\right)$ .

### Criteria for spontaneous change



In the first case  $\Delta H$  is negative and  $\Delta S$  is positive and the process is spontaneous but for the second process both the  $\Delta H$  and  $\Delta S$  are negative and still the process is spontaneous. So here the sign of  $\Delta H$  and  $\Delta S$  do not decide the direction of the spontaneous change. Equilibrium state is the state where there is no spontaneous change can occur to any other state.

From first law of thermodynamics

$$dU = \delta q + \delta w$$

From second law of thermodynamics

$$dS > \frac{\delta q}{T} \quad \text{for spontaneous change}$$

$$TdS > \delta q$$

$$dU - \delta w = \delta q$$

Combining above two equations

$$TdS > dU - \delta w$$

$$0 > dU - \delta w - TdS$$

$$0 > dU + p_{ext}dV - TdS \quad \text{for spontaneous change}$$

All parameters are state functions and controllable.

#### (a) For isolated system

$$q = w = 0 \quad \Delta V = 0 \quad \text{and} \quad \Delta U = 0$$

$$-TdS < 0$$

$$(TdS)_{U,V} > 0$$

**(b) Constant (T, V)**

$$0 > dU + p_{ext}dV - TdS$$

$$0 > d(U - TS) \quad \text{for spontaneous process}$$

For all process

$$0 \geq d(U - TS)$$

Therefore, for a closed system held at constant T and V, the state function  $U-TS$  continuously decreases during the spontaneous, irreversible processes of chemical reaction and matter transport between phases until material equilibrium is reached. At material equilibrium  $d(U - TS)$  equals 0, and  $U-TS$  has reached a minimum. Any spontaneous change at constant T and V away from equilibrium (in either direction) would increase  $U-TS$ , which would naturally imply that a decrease in  $S_{univ}$ . This decrease would violate the second law. The approach to and achievement of material equilibrium is a consequence of second law.

The condition for material equilibrium in a closed system capable of doing only P-V work and held at constant T and V is minimization of system state function  $U-TS$ . This state function is called the Helmholtz free energy, the Helmholtz energy, Helmholtz function or the work function and is symbolized by  $A$ . Arbeit in German means work.

$$A = U - TS$$

$$(dA)_{V,T} < 0$$

**(c) constant S and  $p_{ext}$**

$$0 > dU + p_{ext}dV - TdS$$

$$0 > dU + p_{ext}dV$$

$$0 > d(U + pV)$$

$$0 > dH$$

So the criteria for spontaneous change is

$$(dH)_{S, P} < 0$$

**(d) Constant entropy and volume**

$$0 > dU + p_{ext}dV - TdS$$

$$0 > dU$$

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

$dU$  minimum for a spontaneous change.

**(e) Constant (T, p)**

$$0 > dU + p_{ext}dV - TdS$$

$$0 > d(U + pV) - TdS$$

$$0 > d(H) - TdS$$

Therefore for a material change at constant T and P in a closed system in mechanical and thermal equilibrium and capable of doing only P-V work, we know

$$0 \geq d(H) - TdS$$

where equality sign holds at material equilibrium

Thus the state function  $H - TS$  continuously decreases during material changes at constant T and P until equilibrium is reached. The condition for material equilibrium at constant T and P in a closed system during P-V work only is minimization of the system's state function  $H - TS$ . This state function is called **Gibbs function**, the **Gibbs energy** or **Gibbs free energy**.

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

$$0 > d(G)_{T, p} \text{ for spontaneous process}$$

$$0 = d(G)_{T, p} \text{ for equilibrium process}$$

**Relation of thermodynamic quantity to equation of state ( $p, V, T$ ) data.**



$$dU = TdS - pdV \quad U(S, V)$$

$$H = U + pV \quad dH = dU + pdV + Vdp$$

$$dH = TdS - pdV + pdV + Vdp$$

$$dH = TdS + Vdp \quad H(S, p)$$

$$A = U - TS, \quad dA = dU - TdS - SdT$$

$$dA = TdS - pdV - TdS - SdT$$

$$dA = -SdT - pdV \quad A(T, V)$$

$$G = H - TS$$

$$dG = dH - TdS - SdT$$

$$dG = TdS + Vdp - TdS - SdT$$

$$dG = Vdp - SdT \quad G(p, T)$$

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. These equations are called fundamental equations of thermodynamics. Because  $U$ ,  $H$ ,  $A$ , and  $G$  are state functions, two different equivalent expressions such as those written for  $dU$  here can be formulated:

$$dU = TdS - pdV$$

since  $U(S, V)$ .

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

By comparing terms in the above two equations

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \text{and} \quad \left(\frac{\partial U}{\partial V}\right)_S = -p$$

Similarly  $H(S, p)$

$$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dp$$
$$dH = TdS + Vdp$$

Comparing above two

$$\left(\frac{\partial H}{\partial S}\right)_p = T \quad \text{and} \quad \left(\frac{\partial H}{\partial p}\right)_S = V$$

Similarly  $A(T, V)$

$$dA = \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial A}{\partial V}\right)_T dV$$
$$dA = -SdT - pdV$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \quad \text{and} \quad \left(\frac{\partial A}{\partial V}\right)_T = -p$$

Similarly  $G(T, p)$

$$dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp$$
$$dG = Vdp - SdT$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \quad \text{and} \quad \left(\frac{\partial G}{\partial p}\right)_T = V$$

These expressions state how U, H, A, and G vary with their natural variables. For example, because T and V always have positive values, Equations states that H increases if either the entropy or the pressure of the system increases.

### **Temperature dependence of Gibbs Energy**

The dependence of the Gibbs energy on temperature is expressed in several different ways for convenience in different problems. Since the equilibrium composition of a system depends on the Gibbs energy, to discuss the response of the composition to temperature we need to know how  $G$  varies with temperature. The first relation  $(\partial G/\partial T)_p = -S$ , is our starting point for this discussion. Although it expresses the variation of  $G$  in terms of the entropy, we can express it in terms of the enthalpy by using the definition of  $G$  to write  $S = (H - G)/T$ . Then

$$-S = \frac{(G - H)}{T}$$

$$\left(\frac{\partial G}{\partial T}\right)_p = \frac{(G - H)}{T}$$

Frequently it is important to know how the function  $G/T$  depends on temperature. By the ordinary rule of differentiation, we obtain

$$\left(\frac{\partial(G/T)}{\partial T}\right)_p = \frac{1}{T} \left(\frac{\partial G}{\partial T}\right)_p - \frac{1}{T^2} G$$

Since  $(\partial G/\partial T)_p = -S$

$$\left(\frac{\partial(G/T)}{\partial T}\right)_p = \frac{-(TS + G)}{T^2}$$

Which reduces to **Gibbs- Helmholtz equation**

$$\left(\frac{\partial(G/T)}{\partial T}\right)_p = \frac{-H}{T^2}$$

Since  $\partial(1/T) = -(1/T^2) dT$  ,  $-\partial(1/T)T^2 = dT$ , so replacing  $dT$

$$\left(\frac{\partial(G/T)}{d(1/T)}\right)_p = H$$

Which is another form of **Gibbs- Helmholtz equation**.

### Variation of Gibbs energy with pressure

$$dG = VdP - SdT$$

$$d\bar{G} = \bar{V}dP - SdT$$

For a ideal gas at constant temperature

$$d\bar{G} = \bar{V}dP$$

Integrate on both sides

$$\int_1^2 d\bar{G} = \int_{p_1}^{p_2} \bar{V} dP$$

$$\bar{G}(T, p_2) = \bar{G}(T, p_1) + \int_{p_1}^{p_2} \frac{RT}{p} dP$$

$$\bar{G}(T, p_2) = \bar{G}(T, p_1) + RT \ln \frac{p_2}{p_1}$$

$p_1 = 1 \text{ bar}$  is the reference point

$$\bar{G}(T, p_2) = \bar{G}^0(T, p_1) + RT \ln \frac{p_2}{1 \text{ bar}}$$

Very often this equation is written without writing 1 bar.

G per mol is important called chemical potential  $\bar{G}(T, p) = \mu$ ,  $\bar{G}^0(T, 1 \text{ bar}) = \mu^0$

$$\mu = \mu^0 + RT \ln p_2$$

### Maxwell's equations

We now have the tools to derive some very useful relationships between thermodynamics variables. Maxwell's equations are based on the same principle as was Euler's test for exact differentials, namely that mixed second derivatives of "nice" functions must be equal. Applying this principle to our two new free energy functions we find,

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

$$dA = -SdT -pdV$$

$$\left(\frac{\partial}{\partial V} \left[ \frac{\partial A}{\partial T} \right]_V\right)_T = - \left(\frac{\partial S}{\partial V}\right)_T$$

$$\left(\frac{\partial}{\partial T} \left[ \frac{\partial A}{\partial V} \right]_T\right)_V = - \left(\frac{\partial p}{\partial T}\right)_V$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

One of the applications of the Maxwell's relations is that it connects measure of the equation of the state with other thermodynamic properties.

Consider ideal gas  $pV = nRT$

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V} = \left(\frac{\partial S}{\partial V}\right)_T$$

Consider a system changes from (1) → (2), volume changes from  $V_1$  to  $V_2$  at constant T

$$\Delta S = S(T, V_2) - S(T, V_1)$$

$$\frac{nR}{V} = \left(\frac{\partial S}{\partial V}\right)_T$$

$$\frac{nR}{V} dV = dS$$

On integrating on both sides

$$nR \int_{V_1}^{V_2} \frac{dV}{V} = \Delta S$$

$$nR \ln \frac{V_2}{V_1} = \Delta S$$

(2)

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

$$dG = Vdp - SdT$$

$$\left(\frac{\partial}{\partial T} \left[ \frac{\partial G}{\partial P} \right]_T\right)_P = \left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial}{\partial P} \left[ \frac{\partial G}{\partial T} \right]_p\right)_T = - \left(\frac{\partial S}{\partial P}\right)_T$$

$$\left(\frac{\partial S}{\partial P}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_p \text{ Again equation of the state.}$$

### Mnemonic scheme for thermodynamics

#### Good Professors Have Studied Under Very Fine Teaches

To obtain the differential of a potential, for example  $dU$ , draw two curved arrows toward the potential  $U$  from the two far ends of the inner square, that is,  $P$  and  $T$ . crossing the inner square diagonally, as shown in Figure 1a. These two curved arrows give  $+TdS$  and  $-PdV$ , thus  $dU = TdS - PdV$ . [The variables ( $S$  and  $V$ ) close to the potential ( $U$ ) are with differentials.] The positive or negative sign in front of each term is simply determined by the upward or downward direction of the arrow crossing along the diagonal of the inner square.

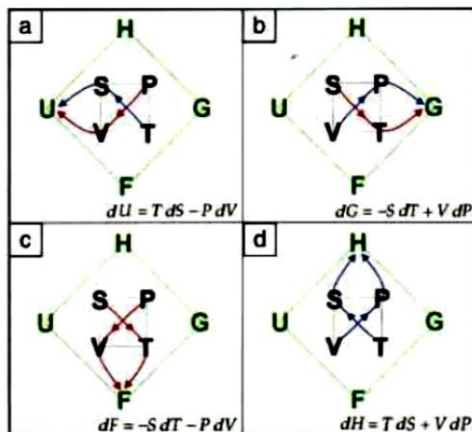


Figure 1:

The variables from the partial differential of a potential with respect to the conjugate variable. This is schematically shown in Figure 2. To obtain  $T$ , draw a curved arrow from  $T$ , and cross the inner square diagonally (thus passing  $S$ ) toward one of the nearby potentials (e.g.  $H$ ). The curved arrow gives  $\left(\frac{\partial H}{\partial S}\right)_p = T$ . This term has a positive sign because the arrow points upward (Figure 2a). The constant  $P$  is shown by the nearby variable with the dotted circle.

Note that the T is at the beginning of the curved arrow, not the end of it (Somewhat backward).

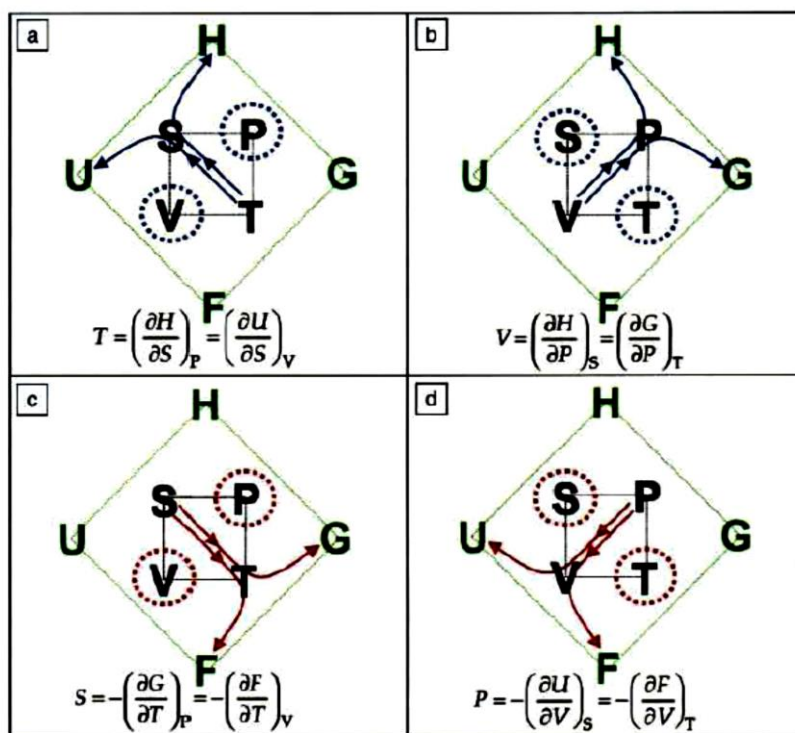


Figure 2:

The Maxwell relations involve only the variables, not the thermodynamic potentials; thus, they can be obtained using the inner (variable) square only without bothering with the outer (potential) square, as shown in Figure 3. In this case, one can start at any corner of the square, going around the square either clockwise or counterclockwise for half a square (including three variables each time). For instance, from T to V to S, it yields the partial derivative of T with respect to V at constant S (left-hand side of Figure 3). The positive or negative sign of the term is again dictated by the upward or downward direction of the arrow connecting the first letter (T) to the third letter (S) (thus crossing the square diagonally). For the case of T to V to S, the arrow is upward, so the term has a positive sign.

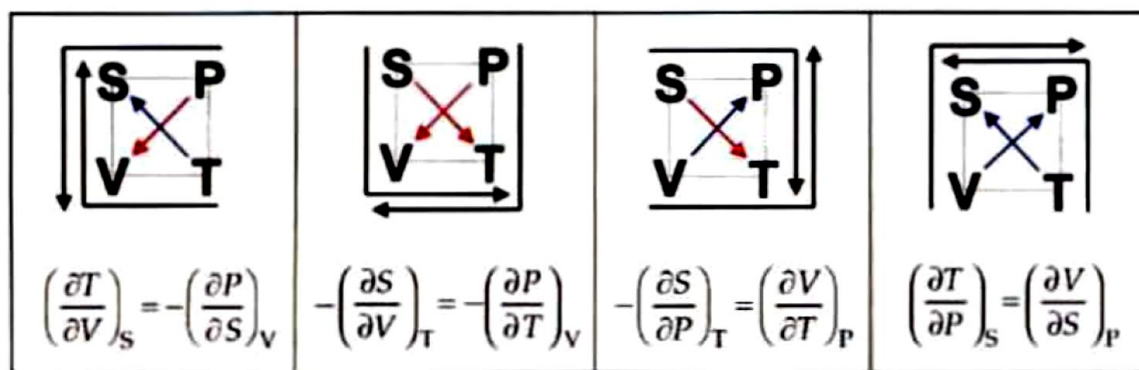


Figure 3:

### Gibbs energy of a reaction mixture

Because reactants are consumed and products are generated in chemical reactions, the expressions derived for state functions such as  $U$ ,  $H$ ,  $S$ ,  $A$ , and  $G$  must be revised to include changes in composition. We focus on  $G$  in the following discussion. For a reaction mixture containing species 1, 2, 3, . . . ,  $G$  is no longer a function of the variables  $T$  and  $P$  only. Because it depends on the number of moles of each species,  $G$  is written in the form  $G = G(T, P, n_1, n_2, n_3, \dots)$ . The total differential  $dG$  is

$$dG = \left(\frac{\partial G}{\partial T}\right)_{p, n_1, n_2, \dots} dT + \left(\frac{\partial G}{\partial p}\right)_{T, n_1, n_2, \dots} dp + \left(\frac{\partial G}{\partial n_1}\right)_{T, p, n_2, \dots} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T, p, n_1, \dots} dn_2$$

$$dG = -S dT + V dp + \mu_1 dn_1 + \mu_2 dn_2 + \dots$$

$$dG = -S dT + V dp + \sum_i \mu_i dn_i$$

$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T, p, n_j}$

 $\partial G$  scales with size and  $\partial n_i$  scales with size and so  $\mu_i$  is intensive

property

It is important to realize that although  $\mu_i$  is defined mathematically in terms of an infinitesimal change in the amount  $dn_i$  of species  $i$ , the chemical potential  $\mu_i$  is the change in the Gibbs energy per mole of substance  $i$  added at constant concentration. These two



requirements are not contradictory. To keep the concentration constant, one adds a mole of substance  $i$  to a huge vat containing many moles of the various species.

On integrating

$$\int_0^G dG = \sum_i \mu_i \int_0^{n_i} dn_i$$

$$G = \sum_i \mu_i n_i$$

Note that because  $\mu_i$  depends on the number of moles of each species present, it is a function of concentration. If the system consists of a single pure substance A,  $G = n_A G_{m,A}$  because G is an extensive quantity

$$\mu_A = \left( \frac{\partial G}{\partial n_A} \right)_{p, T} = \left( \frac{\partial [n_A G_{m, A}]}{\partial n_A} \right)_{p, T} = G_{m, A}$$

showing that  $\mu_A$  is an intensive quantity equal to the molar Gibbs energy of A for a pure substance

This can be understood by assuming that the chemical potential for species  $i$  has the values  $\mu_i^I$  in region I, and  $\mu_i^{II}$  in region II of a given mixture with  $\mu_i^I > \mu_i^{II}$ . If  $dn_i$  moles of species  $i$  are transported from region I to region II at constant T and P, the change in G is given by

$$dG = -\mu_i^I dn_i + \mu_i^{II} dn_i = (\mu_i^{II} - \mu_i^I) dn_i < 0$$

Because  $dG < 0$  this process is a spontaneous process. For a given species, transport will occur spontaneously from a region of high chemical potential to one of low chemical potential. The flow of material will continue until the chemical potential has the same value in all regions of the mixture. Note the analogy between this process and the flow of mass in a gravitational potential or the flow of charge in an electrostatic potential. Therefore, the term chemical potential is appropriate. In this discussion, we have defined a new criterion for equilibrium in a multicomponent mixture: at equilibrium, the chemical potential of each species is the same throughout a mixture.

### Representations of chemical potential in other forms

$$H = G + TS$$

$$dH = dG + d(TS)$$

$$dH = -S dT + VdP + \sum_i \mu_i dn_i + TdS + SdT$$

$$dH = VdP + \sum_i \mu_i dn_i + TdS$$

$$\mu_i = \left( \frac{\partial H}{\partial n_i} \right)_{S, p, n_j}$$

$$A = G - VP$$

$$dA = dG - Vdp - pdV$$

$$dA = -S dT + VdP + \sum_i \mu_i dn_i + -Vdp - pdV$$

$$dA = -S dT + \sum_i \mu_i dn_i - pdV$$

$$\mu_i = \left( \frac{\partial A}{\partial n_i} \right)_{T, V, n_j}$$

$$dU = dA + TdS + SdT$$

$$-S dT + \sum_i \mu_i dn_i - pdV + TdS + SdT = dU$$

$$\sum_i \mu_i dn_i - pdV + TdS = dU$$

$$\mu_i = \left( \frac{\partial U}{\partial n_i} \right)_{S, V, n_j}$$

### The Gibbs-Duhem equation

The Gibbs energy is given by

$$dG = -SdT + VdP + \sum_i \mu_i dn_i$$

For a binary solution at constant temperature and pressure

$$dG = \mu_1 dn_1 + \mu_2 dn_2$$

Imagine starting with an infinitesimally small amount of a solution at constant T and P. The amount is gradually increased at constant composition. Because of this restriction, the chemical potentials are unchanged as the size of the system is changed. Therefore, the  $\mu_i$  can be taken out of the integral

$$\int_0^G dG' = \mu_1 \int_0^{n_1} dn'_1 + \mu_2 \int_0^{n_2} dn'_2$$

$$G = \mu_1 n_1 + \mu_2 n_2$$

The primes have been introduced to avoid using the same symbol for the integration variable and the upper limit. The total differential of the last equation is

$$dG = \mu_1 dn_1 + \mu_2 dn_2 + n_1 d\mu_1 + n_2 d\mu_2$$

Equating both equations for  $dG$ , we get Gibbs-Duhem equation for a binary solution which can be written in the form

$$n_1 d\mu_1 + n_2 d\mu_2 = 0$$

This equation states that the chemical potentials of the components in a binary solution are not independent. If the change in the chemical potential of the first component is  $d\mu_1$ , the change of the chemical potential of the second component is given by

$$d\mu_2 = -\frac{n_1 d\mu_1}{n_2}$$

## Partial molar quantities

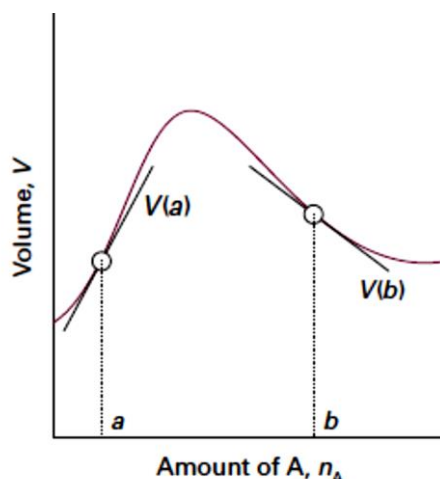
### (a) Partial molar volume

Imagine a huge volume of pure water at 25°C. When a further 1 mol H<sub>2</sub>O is added, the volume increases by 18 cm<sup>3</sup> and we can report that 18 cm<sup>3</sup> mol<sup>-1</sup> is the molar volume of pure water. However, when we add 1 mol H<sub>2</sub>O to a huge volume of pure ethanol, the volume increases by only 14 cm<sup>3</sup>. The reason for the different increase in volume is that the volume occupied by a given number of water molecules depends on the identity of the molecules that surround them. In the latter case there is so much ethanol present that each H<sub>2</sub>O molecule is surrounded by ethanol molecules. The network of hydrogen bonds that normally hold H<sub>2</sub>O molecules at certain distances from each other in pure water does not form. The packing of the molecules in the mixture results in the H<sub>2</sub>O molecules increasing the volume by only 14 cm<sup>3</sup>. The quantity 14 cm<sup>3</sup> mol<sup>-1</sup> is the partial molar volume of water in pure ethanol. In general, the partial molar volume of a substance A in a mixture is the change in volume per mole of A added to a large volume of the mixture. The partial molar volumes of the components of a mixture vary with composition because the environment of each type of molecule changes as the composition changes from pure A to pure B. It is this changing molecular environment, and the consequential modification of the forces acting between molecules, that results in the variation of the thermodynamic properties of a mixture as its composition is changed.

The partial molar volume,  $V_J$  of the substance J at general composition is defined as follows

$$V_J = \left( \frac{\partial V}{\partial n_J} \right)_{p,T,n'}$$

where the subscript  $n'$  signifies that the amounts of all other substances present are constant. The partial molar volume is the slope of the plot of the total volume as the amount of J is changed, the pressure, temperature, and amount of the other components being constant.



**Figure:** The partial molar volume of a substance is the slope of the variation of the total volume of the sample plotted against the composition. In general, partial molar quantities vary with the composition, as shown by the different slopes at the compositions a and b. Note that the partial molar volume at b is negative: the overall volume of the sample decreases as A is added.

$$dV = \left( \frac{\partial V}{\partial n_A} \right)_{p,T,n_B} dn_A + \left( \frac{\partial V}{\partial n_B} \right)_{p,T,n_A} dn_B$$

The definition implies that, when the composition of the mixture is changed by the addition of  $dn_A$  of A and  $dn_B$  of B, then the total volume of the mixture changes by

$$dV = V_A dn_A + V_B dn_B$$

Provided the relative composition is held constant as the amounts of A and B are increased, we can obtain the final volume by integration

$$\begin{aligned} V &= \int_0^{n_A} V_A dn_A + \int_0^{n_B} V_B dn_B = V_A \int_0^{n_A} dn_A + V_B \int_0^{n_B} dn_B \\ &= V_A n_A + V_B n_B \end{aligned}$$

Partial molar volumes can be measured in several ways. One method is to measure the dependence of the volume on the composition and to fit the observed volume to a function of the amount of the substance. Once the function has been found, its slope can be determined at any composition of interest by differentiation.

Molar volumes are always positive, but partial molar quantities need not be. For example, the limiting partial molar volume of  $\text{MgSO}_4$  in water (its partial molar volume in the limit of zero concentration) is  $-1.4 \text{ cm}^3 \text{ mol}^{-1}$ , which means that the addition of 1 mol  $\text{MgSO}_4$  to a large volume of water results in a decrease in volume of  $1.4 \text{ cm}^3$ . The mixture contracts because the salt breaks up the open structure of water as the  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  ions become hydrated, and it collapses slightly.

### (b) Partial molar Gibbs energies

The concept of a partial molar quantity can be extended to any extensive state function. For a substance in a mixture, the chemical potential is defined as the partial molar Gibbs energy:

$$\mu_J = \left( \frac{\partial G}{\partial n_J} \right)_{p, T, n'}$$

That is, the chemical potential is the slope of a plot of Gibbs energy against the amount of the component J, with the pressure and temperature (and the amounts of the other substances) held constant

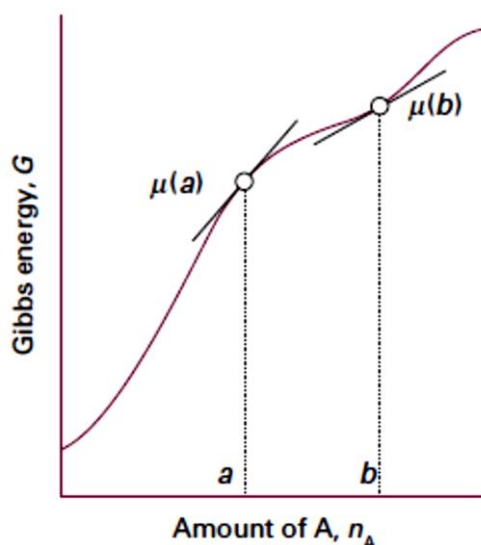


Fig. The chemical potential of a substance is the slope of the total Gibbs energy of a mixture with respect to the amount of substance of interest. In general, the chemical potential varies with composition, as shown for the two values at a and b. In this case, both chemical potentials are positive.

Dr. Biju A R

For a pure substance we can write  $G = n_j G_{j,m}$  and from eqn 5.4 obtain  $\mu_j = G_{j,m}$  in this case, the chemical potential is simply the molar Gibbs energy of the substance.

The total Gibbs energy of a binary mixture is

$$G = n_A \mu_A + n_B \mu_B$$

where  $\mu_A$  and  $\mu_B$  are the chemical potentials at the composition of the mixture. That is, the chemical potential of a substance in a mixture is the contribution of that substance to the total Gibbs energy of the mixture. Because the chemical potentials depend on composition (and the pressure and temperature), the Gibbs energy of a mixture may change when these variables change, and, for a system of components A, B, etc., the equation  $dG = Vdp - SdT$  becomes

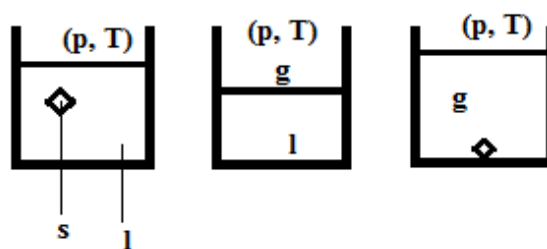
$$dG = V dp - S dT + n_A d\mu_A + n_B d\mu_B + \dots$$

This expression is the fundamental equation of chemical thermodynamics. Its implications and consequences are explored and developed in this and the next two chapters.

At constant pressure and temperature

$$dG = \mu_A dn_A + \mu_B dn_B + \dots$$

### Phase equilibrium in one component systems

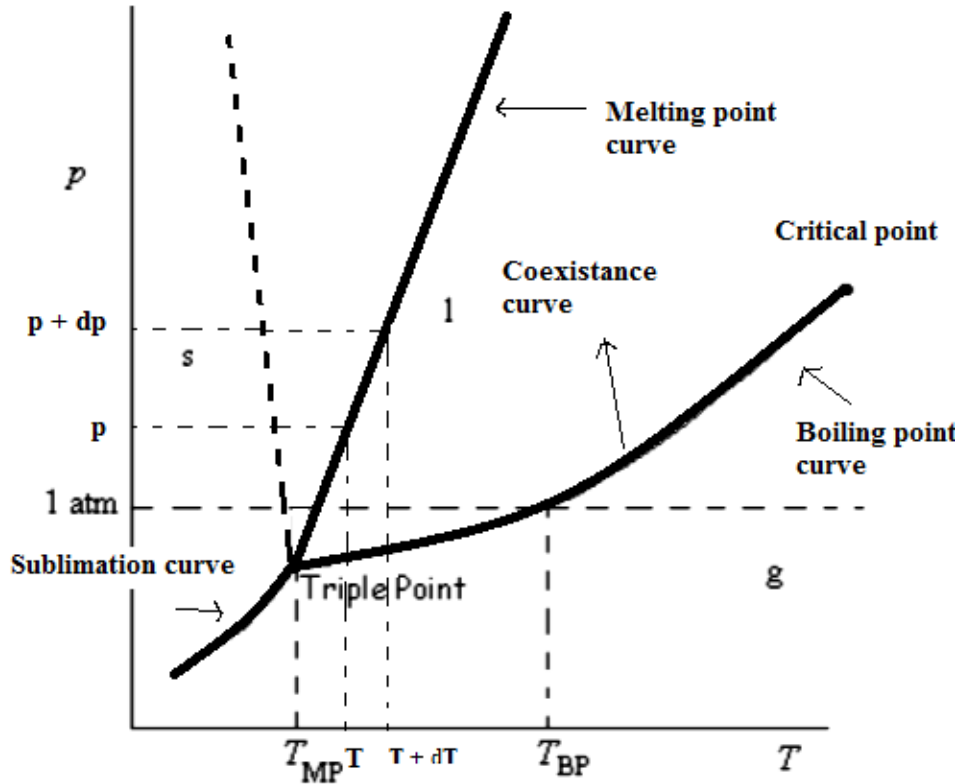


We are going to concentrate on Gibbs free energy  $G$  and  $G/n = \mu$ , chemical potential. At equilibrium  $\mu$  is identical in every phase. If not, molecules will go into phase with lower  $\mu$ .

Ice- water equilibrium

$$\mu_s(T, p) = \mu_l(T, p)$$

$T = 0\text{ }^{\circ}\text{C}$  and  $p = 1\text{ bar}$ . Then at equilibrium ice and water coexists. At some  $(T, p)$   $\mu_s > \mu_l$  then ice melts. If  $\mu_l > \mu_s$ , then ice forms and water freezes. All these results we can summarize in phase diagrams.



Understanding  $p(T)$  or  $T(p)$  along coexistence curve two phases are there  $\alpha$  and  $\beta$  ( s, l or g)

$$\mu_{\alpha}(T, P) = \mu_{\beta}(T, P)$$

Now two points  $T$  and  $T + dT$

$$T \rightarrow T + dT$$

$$p \rightarrow p + dp$$

$$\mu_{\alpha} \rightarrow \mu_{\alpha} + d\mu_{\alpha}$$

$$\mu_{\beta} \rightarrow \mu_{\beta} + d\mu_{\beta}$$

$$d\mu_{\alpha} = d\mu_{\beta}$$

$$d\mu = d\bar{G} = -\bar{S}_{\alpha}dT + \bar{V}_{\alpha}dp = -\bar{S}_{\beta}dT + \bar{V}_{\beta}dp$$

$$(\bar{S}_{\beta} - \bar{S}_{\alpha}) dT = (\bar{V}_{\beta} - \bar{V}_{\alpha}) dp$$



$$\begin{aligned} \left(\frac{dp}{dT}\right)_{\text{coexistence}} &= \frac{\bar{S}_\beta - \bar{S}_\alpha}{\bar{V}_\beta - \bar{V}_\alpha} \\ &= \left(\frac{\Delta S}{\Delta V}\right)_{\alpha \rightarrow \beta} \end{aligned}$$

These are the slopes of coexistence curve

$$\bar{G} = \bar{H} - T\bar{S}$$

$$\bar{H}_\alpha - T\bar{S}_\alpha = \bar{H}_\beta - T\bar{S}_\beta$$

$$T(\bar{S}_\beta - \bar{S}_\alpha) = \bar{H}_\beta - \bar{H}_\alpha$$

$$\Delta H = T(\Delta S)_{\alpha \rightarrow \beta}$$

$$\left(\frac{dp}{dT}\right)_{\text{coexistence}} = \left(\frac{\Delta H}{T\Delta V}\right)_{\alpha \rightarrow \beta}$$

The above expression is called Clapeyron equation

**(a) The solid–liquid boundary**

$$\left(\frac{dp}{dT}\right)_{\text{coexistence}} = \left(\frac{\Delta_{\text{fus}}H}{T\Delta_{\text{fus}}V}\right)$$

where  $\Delta_{\text{fus}}V$  is the change in molar volume that occurs on melting. The enthalpy of melting is positive (the only exception is helium-3) and the volume change is usually positive and always small. Consequently, the slope  $dp/dT$  is steep and usually positive.

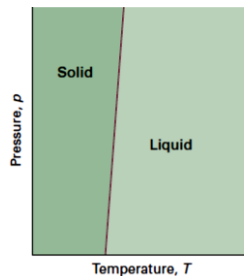


Figure: A typical solid–liquid phase boundary slopes steeply upwards. This slope implies that, as the pressure is raised, the melting temperature rises. Most substances behave in this way.

**(b) The liquid-vapour boundary**

The Clapeyron equation for the liquid vapour boundary is

$$\left(\frac{dp}{dT}\right)_{coexistence} = \left(\frac{\Delta_{vap}H}{T\Delta_{vap}V}\right)$$

The enthalpy of vaporization is positive;  $\Delta_{vap}V$  is large and positive. Therefore,  $dp/dT$  is positive, but it is much smaller than for the solid–liquid boundary. It follows that  $dT/dp$  is large, and hence that the boiling temperature is more responsive to pressure than the freezing temperature.

Because the molar volume of a gas is so much greater than the molar volume of a liquid, we can write  $\Delta_{vap}V \approx V_m(g)$ . Moreover, if the gas behaves perfectly,  $\bar{V}(g) = RT/p$ . These two approximations turn the exact Clapeyron equation into

$$\frac{dp}{dT} = \frac{\Delta_{vap}\bar{H}}{T(RT/p)}$$

which rearrange into Clausius-Clapeyron equation for the variation of vapour pressure with temperature. The Clausius–Clapeyron equation (which is an approximation) is important for understanding the appearance of phase diagrams, particularly the location and shape of the liquid–vapour and solid–vapour phase boundaries. It lets us predict how the vapour pressure varies with temperature and how the boiling temperature varies with pressure.

$$\left(\frac{dp}{p}\right)_{sub\ vap} = \frac{\Delta_{vap}\bar{H}}{RT^2} dT$$

For instance, if we also assume that the enthalpy of vaporization is independent of temperature, this equation can be integrated as follows:

$$\int_{p_1}^{p_2} \frac{dp}{p} = \frac{\Delta\bar{H}}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

$$\log P_2 - \log P_1 = -\frac{\Delta H}{R} \left(\frac{1}{T}\right)_{T_1}^{T_2}$$

$$\log \frac{P_2}{P_1} = -\frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\log \frac{P_2}{P_1} = \frac{\Delta H}{R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)$$

This is called Clausius-Clapeyron equation.

The above equation can be used for calculating the molar heat of vaporization  $\Delta_{vap}\bar{H}$  of a liquid if we know the vapour pressure at two temperatures. Further if  $\Delta_{vap}\bar{H}$  is known, vapour pressure at desired temperature can be calculated from the knowledge of a single value of vapour pressure at a given temperature.

**(c) The solid–vapour boundary**

The only difference between this case and the last is the replacement of the enthalpy of vaporization by the enthalpy of sublimation,  $\Delta_{sub}H$ . Because the enthalpy of sublimation is greater than the enthalpy of vaporization (recall that  $\Delta_{sub}H = \Delta_{fus}H + \Delta_{vap}H$ ), the equation predicts a steeper slope for the sublimation curve than for the vaporization curve at similar temperatures, which is near where they meet at the triple point

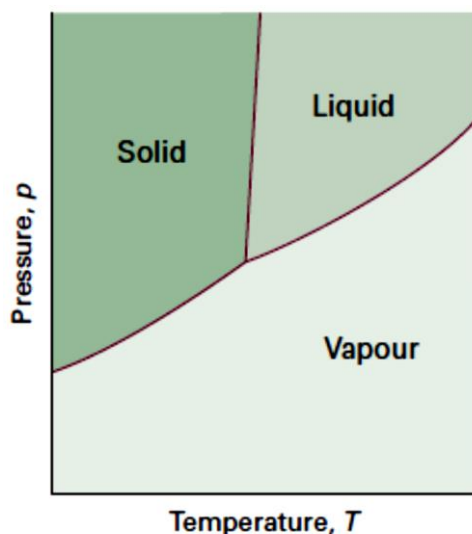


Figure : Near the point where they coincide (at the triple point), the solid–gas boundary has a steeper slope than the liquid–gas boundary because the enthalpy of sublimation is greater than the enthalpy of vaporization and the temperatures that occur in the Clausius–Clapeyron equation for the slope have similar values.

### Third Law of Thermodynamics

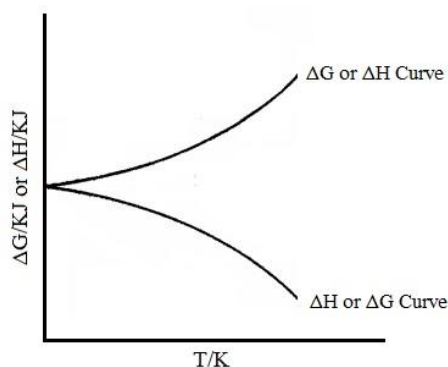
At absolute zero of temperature, the entropy of every substance may become zero and it does become zero in the case of a perfectly crystalline substance.

### The Nernst Heat theorem

Consider Gibbs-Helmholts equation

$$\Delta G - \Delta H = T \left( \frac{\partial \Delta G}{\partial t} \right)_p$$

Where  $\Delta G$  is the change in free energy and  $\Delta H$  is the change in enthalpy accompanying any process including the chemical reaction. It is seen that at absolute zero  $\Delta G = \Delta H$



By measuring EMF of cell at different temperatures, found that the value of  $\left( \frac{\partial \Delta G}{\partial t} \right)_p$  decreases with decrease in temperature and concluded that  $\Delta G$  and  $\Delta H$  tend to approach each other more closely as the temperature is lowered. The value of  $\left( \frac{\partial \Delta G}{\partial t} \right)_p$  approaches zero gradually as the temperature is lowered towards absolute zero. This is known as **Nernst Heat theorem**.

Mathematically theorem may be expressed as.

$$\lim_{T \rightarrow 0} \left( \frac{\partial \Delta G}{\partial t} \right)_p = \lim_{T \rightarrow 0} \left( \frac{\partial \Delta H}{\partial t} \right)_p = 0$$

### Determination of absolute entropy of solids, liquids and gases

We know that at constant pressure

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

By third law of thermodynamics for a perfectly crystalline sample at absolute entropy  $S = 0$

$$\int_{S=0}^{S=S} dS = \int_{T=0}^{T=T} C_p \frac{dT}{T}$$

$$S_T = \int_0^T C_p \frac{dT}{T}$$

Where  $S_T$  is the absolute entropy of the crystalline solid examination at the temperature  $T$

Since it is not possible to obtain the value of  $C_p$  at the absolute zero, heat capacities are measured up to as low temperature as possible like 15 K and value at absolute zero is obtained by extrapolation. Absolute entropy up to 15 K is calculated by Debye  $T^3$  law. Thus

$$S_T = \int_0^{T^*} C_p \frac{dT}{T} + \int_{T^*}^T C_p \frac{dT}{T}$$

Where  $T^* = 15 \text{ K}$ .

$C_p$  up to 15 K is obtained by Debye  $T^3$  law

$$S_T = \int_0^{T^*} aT^3 \frac{dT}{T} + \int_{T^*}^T C_p \frac{dT}{T}$$

$$S_T = \int_0^{T^*} aT^2 dT + \int_{T^*}^T C_p \frac{dT}{T}$$

$$S_T = a \left( \frac{T^*}{3} \right)^3 + \int_{T^*}^T C_p \frac{dT}{T}$$

Suppose it is required to determine absolute entropy a gas at 25 °C under atmospheric pressure. This would be equal to the sum of following reversible process. It is assumed that solid exists in two allotropic forms  $\alpha$  and  $\beta$

1. Heating the sample form absolute zero to  $T^*$

$$\Delta S_1 = a \left( \frac{T^*}{3} \right)^3$$

2. Heating crystalline solid from  $T^*$  to  $T_{tra}$ . Where  $T_{tra}$  is the transition temperature at which the crystalline solid changes from  $\alpha$  to  $\beta$

$$\Delta S_2 = \int_{T^*}^T C_{p,s}(\alpha) \frac{dT}{T}$$

Where  $C_{p,s}(\alpha)$  is the heat capacity of the solid in allotropic form  $\alpha$ .

3. Transition of solid from allotropic form  $\alpha$  to allotropic form  $\beta$

$$\Delta S_3 = \frac{\Delta H_{tran}}{T_{tran}}$$

Where  $\Delta H_{tran}$  is the molar heat enthalpy for transition.

4. Heating the solid in allotropic form  $\beta$  to up to its fusion point  $T_f$

$$S_4 = \int_{T_{tran}}^{T_f} C_{p,s}(\beta) \frac{dT}{T}$$

Where  $C_{p,s}(\beta)$  is the heat capacity of the solid in allotropic form  $\beta$ .

5. Changing the allotropic form  $\beta$  into liquid state at fusion point

$$S_5 = \frac{\Delta H_f}{T_f}$$

6. Heating the liquid from its freezing point  $T_f$  to its boiling point  $T_b$

$$S_6 = \int_{T_f}^{T_b} C_{p,l} \frac{dT}{T}$$

7. Changing the liquid into gaseous state at the temperature  $T_b$

$$S_7 = \frac{\Delta H_v}{T_b}$$

8. Heating the gas from  $T_b$  to the required temperature at 298.15 K

$$S_8 = \int_{T_b}^{298.15} C_{p,g} \frac{dT}{T}$$

Dr. Biju A R

Where  $C_{p,g}$  is the heat capacity of the substance at gaseous state. So the absolute entropy of the gas at 298.15 K is equal to the sum of 8 steps

$$\Delta S_T = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 + \Delta S_5 + \Delta S_6 + \Delta S_7 + \Delta S_8$$