Contents

1 Thermodynamic Potentials

By the second law of thermodynamics, an isolated system during a spontaneous change reaches an equilibrium state characterized by maximum entropy:

$$dS = 0, \quad S = S_{\text{max}} \tag{1.1}$$

On the other hand, it is known from mechanics, electrodynamics and quantum mechanics that a system which is not isolated minimizes its energy. An interacting thermodynamic system always exchanges heat or perform work on the surroundings during a spontaneous change to minimize its internal energy. However, the entropy of the system plus the surroundings, which could be thought as a whole an isolated system, always increases. Thus, a non-isolated system at constant entropy always leads to a state of minimum energy.

1.1 Entropy as a thermodynamic potential:

Both entropy and the internal energy are state functions. If they are known as function of state variables of an isolated system then all other thermodynamic quantities are completely known. Consider the internal energy $E = E(S, V, N)$ then, the differential form of energy is

$$dE = TdS - PdV + \mu dN \tag{1.2}$$

So, the temperature and pressure are known as functions of other state variables

$$T = \left(\frac{\partial E}{\partial S}\right)_{V,N}, \quad -P = \left(\frac{\partial E}{\partial V}\right)_{S,N}, \quad \mu = \left(\frac{\partial E}{\partial N}\right)_{S,V} \tag{1.3}$$

Similarly, consider the entropy $S = S(E, N, V)$, then

$$TdS = dE + PdV - \mu dN \tag{1.4}$$

and the temperature and pressure can be found as

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}, \quad P = T\left(\frac{\partial S}{\partial V}\right)_{E,N}, \quad \mu = -T\left(\frac{\partial S}{\partial N}\right)_{E,V} \tag{1.5}$$

The entropy and the internal energy then can be calculated as functions of the state variables form the equation of state. Since the equilibrium state of the system is given by a maximum of the entropy as a function of (E, V), it gives information about the most stable equilibrium state of the system as potential energy does in mechanics.

As the difference in potential energy defines the direction of a natural process in mechanics, the entropy difference determines the direction of a spontaneous change in an isolated system. Thus, the entropy can be called as a thermodynamic potential.

1.2 Enthalpy as a thermodynamic potential:

The enthalpy of a system is defined as

$$H = E + PV \tag{1.6}$$

the differential form is

$$dH = dE + PdV + VdP \quad \Longrightarrow \quad dH = TdS + VdP + \mu dN \tag{1.7}$$

Knowing the enthalpy $H = H(S, P, N)$, the state variables can be calculated as

$$T = \left(\frac{\partial H}{\partial S}\right)_{P,N}, \quad V = \left(\frac{\partial H}{\partial P}\right)_{S,N}, \quad \mu = \left(\frac{\partial H}{\partial N}\right)_{S,P} \tag{1.8}$$

Consider an isolated system at constant pressure. Process at constant pressure are of special interest in chemistry since most of the chemical reactions occur under constant atmospheric pressure. In an isolated-isobaric system, $\delta Q = 0$ and P is constant, thus

$$dE + PdV = 0 \quad \Longrightarrow \quad d(E + PV) = 0 \quad \Longrightarrow \quad dH = 0 \tag{1.9}$$

In a spontaneous process of an adiabatic-isobaric system, the equilibrium corresponds to the minimum of the enthalpy

$$dH = 0, \quad H(S, P) = H_{\text{min}} \tag{1.10}$$

1.3 Helmholtz free energy as a thermodynamic potential:

The Helmholtz potential (free energy) is defined as

$$F = E - TS \tag{1.11}$$

the differential form

$$dF = dE - SdT - TdS \quad \Longrightarrow \quad dF = -SdT - PdV + \mu dN \tag{1.12}$$

since $dE = TdS - PdV + \mu dN$. Thus, knowing $F = F(T, V, N)$, S, P and μ could be determined as

$$-S = \left(\frac{\partial F}{\partial T}\right)_{V,N}, \quad -P = \left(\frac{\partial F}{\partial V}\right)_{T,N}, \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} \tag{1.13}$$

The Helmholtz potential is useful in defining the equilibrium of a non-isolated system in contact with heat bath at constant temperature T. The system is interacting with the heat bath through heat exchange only. Consider an arbitrary isothermal transformation of this system from a state A to state B. By the second law , one have

$$\int_A^B \frac{dQ}{T} \leq S(B) - S(A) \tag{1.14}$$

Since T is constant

$$\frac{\Delta Q}{T} \leq \Delta S \tag{1.15}$$

where ΔQ is the amount of heat absorbed during the transformation and $\Delta S = S(B) - S(A)$. Using the first law, the inequality could be written as

$$\Delta W \leq -\Delta E + T\Delta S \quad \Longrightarrow \quad \Delta W \leq -\Delta F \tag{1.16}$$

where ΔW is the work done by the system. Thus, the equilibrium of an isothermal system which does not perform work (mechanically isolated) always looks for a minimum of Helmholtz potential. Irreversible process happen spontaneously, until the minimum

$$dF = 0, \quad F = F_{\min} \tag{1.17}$$

is reached.

1.4 Gibbs free energy as a thermodynamic potential:

The Gibb's potential (free energy) is defined as

$$G = E - TS + PV = F + PV \tag{1.18}$$

the differential form

$$dG = -SdT + VdP + \mu dN \tag{1.19}$$

since $E = TS - PV + \mu N$ for a system attached with heat bath as well as with a bariostat. System exchanges heat and does some work due to volume expansion at constant pressure. The thermodynamic variables can be obtained in terms of $G(P, T, N)$ as

$$-S = \left(\frac{\partial G}{\partial T}\right)_{P,N}, \quad V = \left(\frac{\partial G}{\partial P}\right)_{T,N}, \quad \mu = \left(\frac{\partial G}{\partial N}\right)_{T,P} \tag{1.20}$$

Notice that the chemical potential μ can be defined as Gibb's free energy per particle. Consider a system at constant pressure and temperature. For isothermal process,

$$\Delta W \leq -\Delta F \tag{1.21}$$

as it is already seen. If the pressure remain constant $\Delta W = P\Delta V$, then

$$P\Delta V + \Delta F \leq 0 \quad \Longrightarrow \quad \Delta G \leq 0 \tag{1.22}$$

Thus, a system kept at constant temperature and pressure, the Gibb's free energy never increases and the equilibrium state corresponds to minimum Gibb's potential. Irreversible spontaneous process in an isothermal - isobaric system

$$dG = 0 \quad G = G_{\min} \tag{1.23}$$

are always achieved.

1.5 Grand potential as a thermodynamic potential:

The grand potential is defined as

$$\Phi = E - TS - \mu N = F - \mu N = -PV \tag{1.24}$$

since $E = TS - PV + \mu N$. The system attached with heat bath as well as with a particle reservoir. System exchanges heat with heat bath and exchanges particle with the particle reservoir. Differentially the grand potential can be expressed as

$$\begin{aligned} d\Phi &= dE - TdS - SdT - \mu dN - Nd\mu \\ &= -SdT - PdV - Nd\mu \end{aligned} \tag{1.25}$$

since $dE = TdS - PdV + \mu dN$. The thermodynamic variables are then obtained in terms of $\Phi(V, T, \mu)$ as

$$-S = \left(\frac{\partial \Phi}{\partial T}\right)_{V,\mu}, \quad -P = \left(\frac{\partial \Phi}{\partial V}\right)_{T,\mu}, \quad -N = \left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V} \tag{1.26}$$

Consider an isothermal system at constant chemical potential. For an isothermal system

$$\Delta W \leq -\Delta F \tag{1.27}$$

and $\Delta W = -\mu \Delta N$ since μ is constant and the inequality leads to

$$\Delta F - \mu \Delta N \leq 0 \quad \Longrightarrow \quad \Delta \Phi \leq 0 \tag{1.28}$$

Thus, a system kept at constant temperature and chemical potential, the grand potential never increase and the equilibrium state corresponds to minimum grand potential. Irreversible spontaneous process in an isothermal system with constant chemical potential correspond to

$$d\Phi = 0 \quad \Phi = \Phi_{min} \tag{1.29}$$

1.6 Maxwell's relations

A number of relations between the thermodynamic state variables can be obtained since the thermodynamic potentials E, H, F and $G($ also $\Phi)$ are state functions and have exact differentials. We know for exact differentials

$$d\phi = Mdx + Ndy \quad \Longrightarrow \quad \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \tag{1.30}$$

- From

$$dE = TdS - PdV$$
$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \tag{1.31}$$

-

$$dH = TdS + VdP \quad \Longrightarrow \quad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \tag{1.32}$$

-

$$dF = -SdT - PdV \quad \Longrightarrow \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{1.33}$$

-

$$dG = -SdT + VdP \quad \Longrightarrow \quad -\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \tag{1.34}$$

1.7 Response functions

1.7.1 Definitions

A great deal can be learned about a macroscopic system through its response to various changes in externally controlled parameters. Important response functions for a PVT system are the specific heats at constant volume and pressure,

$$\begin{aligned} C_V &= \left(\frac{đQ}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V \\ C_P &= \left(\frac{đQ}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P \end{aligned} \tag{1.35}$$

The isothermal and adiabatic compressibilities,

$$\begin{aligned} K_T &= -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \\ K_S &= -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S \end{aligned} \tag{1.36}$$

and the coefficient of thermal expansion

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N} \tag{1.37}$$

this can be written as

$$\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V}\left(\frac{\partial^2 G}{\partial T \partial P}\right) \tag{1.38}$$

1.7.2 Relations between the response function

Intuitively, we expect the specific heats and compressibilities to be positive and $C_P > C_V, K_T > K_S$. In this section we derive relations between these response functions. The intuition that the response functions are positive will be justified in the following section in which we discuss thermodynamic stability. We begin with the assumption that the entropy has been expressed in terms of T and V and that the number of particles is kept fixed. Then

$$\begin{aligned}
dS &= \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \\
T\left(\frac{\partial S}{\partial T}\right)_P &= T\left(\frac{\partial S}{\partial T}\right)_V + T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \qquad (1.39) \\
C_P - C_V &= T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P
\end{aligned}$$

We now use the Maxwell relations and the chain rule

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial x}{\partial y}\right)_z = -1 \tag{1.40}$$

We get

$$\begin{aligned} \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V &= -\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \\ C_P - C_V = -T\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P^2 &= \frac{TV}{K_T}\alpha^2 \end{aligned} \tag{1.41}$$

In a similar way we obtain a relation between the compressibilities K_T and K_S . Assume that the volume V has been obtained as function of S and P.

Then we get

$$\begin{aligned} dV &= \left(\frac{\partial V}{\partial P}\right)_S dP + \left(\frac{\partial V}{\partial S}\right)_P dS \\ -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T &= -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S - \frac{1}{V}\left(\frac{\partial V}{\partial S}\right)_P \left(\frac{\partial S}{\partial P}\right)_T \\ K_T - K_S &= -\frac{1}{V}\left(\frac{\partial V}{\partial S}\right)_P \left(\frac{\partial S}{\partial P}\right)_T \end{aligned} \tag{1.42}$$

The Maxwell relation and

$$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial S}{\partial T}\right)_P^{-1}$$

gives

$$K_T - K_S = \frac{TV}{C_P}\alpha^2 \tag{1.43}$$

Now we have useful relations

$$C_P\left(K_T - K_S\right) = K_T\left(C_P - C_V\right) = TV\alpha^2 \tag{1.44}$$

And

$$\frac{C_P}{C_V} = \frac{K_T}{K_S} \tag{1.45}$$

1.8 Thermodynamics of a magnetic system

In order to study magnetic properties of matter one requires the expression for the work of magnetizing a material. One needs to be careful in defining precisely the system and the processes in order to calculate magnetic work done. Let us assume that the effects of pressure and volume on a magnetic system is negligible.

1.8.1 Definition of potentials

The thermodynamic parameters of a magnetic system are going to be the external magnetic induction B, total magnetization M and temperature T instead of P, V and T of a fluid system. The first law of thermodynamics: the differential change in internal energy E for a reversible change of state can be written in two different but equivalent forms as

$$dE = TdS - MdB \tag{1.46}$$

or

$$dE = TdS + BdM \tag{1.47}$$

we will use the SECOND form

We define other state functions and thermodynamic potentials such as enthalpy $H(N, S, B)$, the Helmholtz free energy $F(N, M, T)$ and the Gibbs free energy $G(N, B, T)$. The definitions of these thermodynamics state functions and differential change in a reversible change of state are given by

$$\begin{aligned}
H(N,S,B) &= E - MB && \text{and} \quad dH = TdS - MdB \\
F(N,M,T) &= E - TS && \text{and} \quad dF = -SdT + BdM \\
G(N,B,T) &= E - TS - MB && \text{and} \quad dG = -SdT - MdB
\end{aligned} \tag{1.48}$$

where explicit N dependence is also avoided. If one wants to take into account of number of particles there must be another term μdN in all differential forms of the state functions. It can be noticed that the thermodynamic relations of a magnetic system can be obtained from those in fluid system if V is replaced by $-M$ and P is replaced by B.

The thermodynamic parameters can be obtained as

$$T = \left(\frac{\partial E}{\partial S}\right)_M \quad \text{or} \quad T = \left(\frac{\partial H}{\partial S}\right)_B \tag{1.49}$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_M \quad \text{or} \quad S = -\left(\frac{\partial G}{\partial T}\right)_B \tag{1.50}$$

$$B = \left(\frac{\partial E}{\partial M}\right)_S \quad \text{or} \quad B = \left(\frac{\partial F}{\partial M}\right)_T \tag{1.51}$$

$$M = -\left(\frac{\partial H}{\partial B}\right)_S \quad \text{or} \quad M = -\left(\frac{\partial G}{\partial B}\right)_T \tag{1.52}$$

1.8.2 Maxwell relations for magnetic systems

-
$$dE = TdS + BdM \quad \Longrightarrow \quad \left(\frac{\partial T}{\partial M}\right)_S = \left(\frac{\partial B}{\partial S}\right)_M \tag{1.53}$$

-
$$dH = TdS - MdB \quad \Longrightarrow \quad \left(\frac{\partial T}{\partial B}\right)_S = -\left(\frac{\partial M}{\partial S}\right)_B \tag{1.54}$$

-
$$dF = -SdT + BdM \quad \Longrightarrow \quad \left(\frac{\partial S}{\partial M}\right)_T = -\left(\frac{\partial B}{\partial T}\right)_M \tag{1.55}$$

-
$$dG = -SdT - MdB \quad \Longrightarrow \quad \left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial M}{\partial T}\right)_B \tag{1.56}$$

1.8.3 Response functions for magnetic systems

The specific heats C_M and C_B are the measures of the heat absorption from a temperature stimulus at constant magnetization and constant external magnetic field respectively. The definition of heat capacities are :

$$\begin{aligned} C_M &= T\left(\frac{\partial S}{\partial T}\right)_M = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_M \\ C_B &= T\left(\frac{\partial S}{\partial T}\right)_P = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_B \end{aligned} \tag{1.57}$$

In case of magnetic systems, instead of isothermal and adiabatic compressibilities one have the isothermal and the adiabatic magnetic susceptibilities

$$\chi_T = \left(\frac{\partial M}{\partial B}\right)_T = -\left(\frac{\partial^2 G}{\partial B^2}\right)_T \tag{1.58}$$

and

$$\chi_S = \left(\frac{\partial M}{\partial B}\right)_S = -\left(\frac{\partial^2 H}{\partial B^2}\right)_S \tag{1.59}$$

where M is the total magnetization and B is the external magnetic field. Note that the normalizing factor of $1/V$ is absent here.

The change of magnetization M with respect to temperature T under constant external magnetic field α_B, is defined as

$$\alpha_B = \left(\frac{\partial M}{\partial T}\right)_B = \left(\frac{\partial^2 G}{\partial T \partial B}\right) \tag{1.60}$$

The response functions are not all independent of one another. It can be shown that

$$C_B/C_M = \chi_T/\chi_S \tag{1.61}$$

Two other relations you can prove are

$$\chi_T \left(C_B - C_M\right) = T\alpha_B^2 \quad \text{and} \quad C_B \left(\chi_T - \chi_S\right) = T\alpha_B^2 \tag{1.62}$$

2 Some applications of thermodynamics

2.1 TdS equations

The entropy of a pure substance can be considered as a function of any two variables, such as T and V; thus,

$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \\ TdS &= T\left(\frac{\partial S}{\partial T}\right)_V dT + T\left(\frac{\partial S}{\partial V}\right)_T dV \end{aligned} \tag{2.1}$$

since $TdS = đQ$ for a reversible isochoric process, it follows that

$$T\left(\frac{\partial S}{\partial T}\right)_V = C_V \tag{2.2}$$

and from the Maxewells relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

$$TdS = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV \tag{2.3}$$

This is the firs TdS equation.

Similarly take entropy as a function of T and P and derive the second TdS equation

$$TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP \tag{2.4}$$

2.2 Internal energy equations

For the internal energy equation we start from

$$dU = TdS - PdV \tag{2.5}$$

and take partial derivative with respect to V keeping T constant

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P \tag{2.6}$$

Using Maxwell's third relation, $(\partial S/\partial V)_T = (\partial P/\partial T)_V$, we get

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \tag{2.7}$$

This equation is very useful.

Similarly taking partial derivative with respect to P both side of the equation $dU = TdS - PdV$ prove that

$$\left(\frac{\partial U}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial P}\right)_T \tag{2.8}$$

2.3 Heat transfer of isothermal expansion of van der Waals gas

Start with

$$TdS = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$$

From van der Waal's equation

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \tag{2.9}$$

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

Hence

$$TdS = C_V dT + RT\frac{dV}{V-b} \tag{2.10}$$

since T is constant, $C_V dT = 0$; and, since the process is reversible, $q = \int Tds$ Therefore,

$$q = RT\int_{V_i}^{V_f} \frac{dV}{V-b} \tag{2.11}$$

Finally

$$q = RT\ln\frac{V_f-b}{V_i-b} \tag{2.12}$$

2.4 Reversible isothermal change of pressure

When T is constant

$$TdS = -T\left(\frac{\partial V}{\partial T}\right)_P dP \quad \text{and so} \quad Q = -T\int\left(\frac{\partial V}{\partial T}\right)_P dP \tag{2.13}$$

The volume expansivity is

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

then

$$Q = -T \int V\beta dP \tag{2.14}$$

In the case of a solid or liquid, V and β do not change much with pressure. So we can take them out of the integration to get

$$Q = -TV\beta \int_{P_i}^{P_f} dP \quad \Longrightarrow \quad Q = -TV\beta\,(P_f - P_i) \tag{2.15}$$

It is seen from this result that, as the pressure is increased isothermally, heat will flow out if β is insositive but that, prossunce with a negative expansivity (such as water between 0 and 4°C, or a rubber band), an isothermal increase of pressure causes an absorption of heat.

If the pressure on 15cm^3 of mercury at 20°C is increased reversibly and isothermally from 0 to 1000atm, the heat transferred will be approximately

$$Q \simeq -TV\beta P_f$$

where $T = 293\text{K}, V = 2 \times 10^{-5}\text{m}^3, \beta = 1.81 \times 10^{-4}\text{K}^{-1}$, and $P_f = 1.01 \times 10^8\text{Pa}$ Hence,

$$
\begin{aligned}
Q &= -(293\mathrm{K})\left(1.5\times10^{-5}\mathrm{m}^3\right)\left(1.81\times10^{-4}\mathrm{K}^{-1}\right)\left(1.01\times10^{8}\mathrm{Pa}\right)\\
&= -80.3\mathrm{N}\cdot\mathrm{m}\\
&= -80.3\mathrm{J}
\end{aligned}
$$

2.5 Internal energy of van der Waal gas

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

and

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

so

$$\left(\frac{\partial U}{\partial V}\right)_T = T\frac{R}{V-b} - \frac{RT}{V-b} + \frac{a}{V^2} = \frac{a}{V^2} \tag{2.16}$$

SO

$$dU = C_V dT + \frac{a}{V^2}dV \tag{2.17}$$

Finally

$$U = \int C_V dT - \frac{a}{V} + \text{const.} \tag{2.18}$$

2.6 Heat capacities of ideal gas

The difference between the heat capacities is given by

$$C_P - C_V = TV\alpha^2/\kappa_T \tag{2.19}$$

where $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ is the volume expansion coefficient and $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ is the isothermal compressibility. Using this relation, the difference between heat capacities of an ideal gas could be easily obtained. For one mole of an ideal gas, the equation of state is $PV = RT$ where R is the universal gas constant. Thus,

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V}\frac{R}{P} = \frac{1}{T} \tag{2.20}$$

and

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V}\left(-\frac{V}{P}\right) = \frac{1}{P} \tag{2.21}$$

so the differences

$$C_P - C_V = TV\left(\frac{1}{T}\right)^2 \frac{1}{1/P} = \frac{PV}{T} = R \tag{2.22}$$

As $T \to 0$, by third law of thermodynamics, the entropy $S \to S_0 = 0$ becomes independent of all parameters like pressure, volume and temperature. Therefore, in the limit $T \to 0$ the heat capacities also tend to zero,

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V \to 0 \quad \text{and} \quad C_P = T\left(\frac{\partial S}{\partial T}\right)_P \to 0 \tag{2.23}$$

This is because of the fact that as $T \to 0$, the system tends to settle down in its nondegenerate ground state. The mean energy of the system then become essentially equal to its ground state energy, and no further reduction of temperature can result in a further reduction of mean energy.

Not only the individual heat capacity goes to zero but also their difference goes to zero as $T \to 0$. Because, the volume expansion coefficient α also goes to zero

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T \to 0 \tag{2.24}$$

However, the compressibility κ_T, a purely mechanical property, remains well-defined and finite as $T \to 0$. Thus,

$$\text{as} \quad T \to 0 \quad C_P - C_V \to 0 \tag{2.25}$$

This is not in contradiction to the ideal gas result $C_P - C_V = R$ because as $T \to 0$, the system approaches its ground state and quantum mechanical effects become very important. Hence the classical ideal gas equation $PV = RT$ is no longer valid as $T \to 0$.

2.7 Gibbs paradox:

An isolated system with two parts of equal volume V each contains N number of molecules of the same monatomic perfect gas at the same temperature T, pressure P. Initially, the two parts were separated by a membrane and then the membrane was removed. The system is allowed to equilibrate. The change in entropy is given by

$$\Delta S = \int \frac{\delta Q}{T} = \frac{1}{T} \int \delta Q \tag{2.26}$$

From first law, for a perfect gas $dE(T) = \delta Q + \delta W = 0$ and thus $\delta Q = -\delta W = PdV$. The volume changes from V to

$2V$ for the each part. Therefore,

$$\begin{aligned}\Delta S &= \frac{1}{T}\int P dV \\ &= Nk_B \int_V^{2V} \frac{dV}{V} + Nk_B \int_V^{2V} \frac{dV}{V} \\ &= 2Nk_B \ln 2 > 0\end{aligned} \tag{2.27}$$

The entropy of the system then may increase indefinitely by putting more and more membranes and removing them. However, the process is reversible. By putting back the membranes one would recover the initial state. According to Clausius theorem, the change in entropy must be $\Delta S = 0$ in a reversible process. This discrepancy is known as Gibb's paradox. The paradox would be resolved only by applying quantum statistical mechanics. The same problem will be discussed again in the next section.

2.8 Radiation:

According to electromagnetic theory, the pressure P of an isotropic radiation field is equal to 1/3 of the energy density:

$$P = u(T)/3 = U(T)/3V \tag{2.28}$$

where V is the volume of the cavity, U is the total energy. Using the thermodynamic principles, one could obtain Stefan's law: $u = aT^4$, where a is a constant.

To do that we will start from the radiation pressure and also take that the total energy of photon gas is proportional to volume.

By the second law $dU = TdS - PdV$, thus

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P \quad \Longrightarrow \quad \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \tag{2.29}$$

since $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ by Maxwell equation. Since $U = u(T)V$

$$\left(\frac{\partial U}{\partial V}\right)_T = u(T) \quad \text{and} \quad \left(\frac{\partial P}{\partial T}\right)_V = \frac{1}{3}\frac{du}{dT} \tag{2.30}$$

Hence

$$u(T) = \frac{T}{3}\frac{du}{dT} - \frac{1}{3}u \quad \Longrightarrow \quad T\frac{du}{dT} = 4u \quad \Longrightarrow \quad u = aT^4 \tag{2.31}$$

where a is a constant.