

# Unit 2: Thermodynamic Potentials

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## Abstract

Thermodynamic Potentials: Enthalpy, Gibbs, Helmholtz and Internal Energy functions, Maxwells relations & applications – Joule-Thompson Effect, Clausius-Clapeyron Equation, Expression for  $(C_P - C_V)$ ,  $C_P/C_V$ , TdS equations

## 1 Deriving the Maxwell Relations

A thermodynamic potential is a quantity used to represent some thermodynamic state in a system. We can define many thermodynamic potentials on a system and they each give a different measure of the ‘type’ of energy the system has. In this chapter, we will consider four such potentials.

Consider a system undergoing some thermodynamic process which we are interested in analysing. Assume that we know that two quantities of that system will be constant throughout the process. Then, if we can find the thermodynamic potential whose natural variables are those quantities, then we can easily analyse the system using that potential.

A natural variable of a thermodynamic potential is special because when the natural variables of a thermodynamic potential are held constant during a process, it means that we can easily use that potential to analyse the process because that thermodynamic potential will be conserved.

### 1.1 Internal Energy

The internal energy of a system is the energy contained in it due to its molecular constitution and motion. It is the sum of kinetic and potential energy of the system. This is excluding any energy from outside of the system (due to any external forces) or the kinetic energy of a system as a whole. This is only the energy of the system due to the motion and interactions of the particles that make up the system.

Let’s consider the first law of thermodynamics, which gives us a differential form for the internal energy:

$$dU = dQ + dW$$

We know that the work done on a system,

$$dW = PdV$$

Additionally, from the second law of thermodynamics, in terms of entropy, we know that the heat transferred is given by:

$$dQ = TdS$$

$$dU = TdS - PdV$$

Taking partial derivatives of the internal energy with respect to S and V,

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

From the above we know that the natural variables of a thermodynamic potentials are the ones which, if kept constant, mean that the potential is conserved through some process. In this case this means that  $dU=0$

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is achieved when  $dS$  and  $dV$  are both zero. So entropy,  $S$ , and volume,  $V$ , are the natural variables of internal energy,  $U$ . Since  $dU$  is a perfect differential,

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

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

## 1.2 Helmholtz Free Energy

The Helmholtz free energy (represented by the letter  $F$ ) of a system is defined as the internal energy of the system minus the product of its entropy and temperature:

$$F = U - TS$$

This represents the amount of useful work that can be obtained from a closed system at constant temperature and volume. Again, I won't spend too long on the uses of this thermodynamic potential.

Let's now find the differential form of this, the same way we did with enthalpy:

$$dF = dU - d(TS) = dU - TdS - SdT$$

Substituting in the differential form of internal energy

$$dU = TdS - PdV$$

$$dF = TdS - PdV - TdS - SdT$$

$$dF = -PdV - SdT$$

This is the differential form of the Helmholtz free energy. We can now immediately see that volume,  $V$ , and temperature,  $T$ , are the natural variables of the Helmholtz free energy,  $F$ . Taking partial derivatives,

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

Since  $dF$  is a perfect differential,

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

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

## 1.3 Enthalpy

Enthalpy (represented by the letter  $H$ ) is a thermodynamic potential of a system, which is equal to the internal energy of the system plus the product of its pressure and volume:

$$H = U + PV$$

This represents the total heat content of a system and is often the preferred potential to use when studying many chemical reactions which take place at constant pressure. This is because when pressure is constant, the change of enthalpy is equal to the change in internal energy of the system.

The differential form is:

$$dH = dU + d(PV) = dU + PdV + VdP$$

$$dU = TdS - PdV$$

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

$$dH = TdS + VdP$$

This is the differential form of enthalpy. We can apply the same idea we applied to internal energy here to find the natural variables of enthalpy. We can see that  $dH=0$  when  $dS$  and  $dP$  are zero. So entropy,  $S$ , and pressure,  $P$ , are the natural variables of enthalpy,  $H$ . Taking partial derivatives,

$$\left( \frac{\partial H}{\partial S} \right)_P = T, \left( \frac{\partial H}{\partial P} \right)_S = V$$

Since  $dH$  is a perfect differential,

$$\frac{\partial}{\partial P} \left( \frac{\partial H}{\partial S} \right)_P = \frac{\partial}{\partial S} \left( \frac{\partial H}{\partial P} \right)_S$$

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

## 1.4 Gibbs free energy

Gibbs free energy (represented by the letter  $G$ ) is used to calculate the amount of work a system can perform at constant temperature and pressure. As such, it is very useful when studying phase transitions, which happen at such conditions. This is defined as the enthalpy of a system minus the product of the temperature and entropy of the system:

$$G = H - TS$$

Finding the differential form of this (as above):

$$dG = dH - d(TS) = dH - TdS - SdT$$

Substituting in the differential form of enthalpy

$$dH = TdS + VdP$$

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

$$dG = VdP - SdT$$

This is the differential form of the Gibbs free energy. We can see that pressure,  $P$ , and temperature,  $T$ , are the natural variables of the Gibbs free energy,  $G$ . entropy,  $S$ , and pressure,  $P$ , are the natural variables of enthalpy,  $H$ . Taking partial derivatives,

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

Since  $dG$  is a perfect differential,

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

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

## 2 Gibb's-Helmholtz Equation

For the Helmholtz's Function:

$$dF = dU - d(TS) = dU - TdS - SdT$$

Substituting in the differential form of internal energy

$$dU = TdS - PdV$$

$$dF = TdS - PdV - TdS - SdT$$

$$dF = -PdV - SdT$$

At constant Volume:

$$dF = -SdT$$

Taking partial derivatives ,

$$\left( \frac{\partial F}{\partial T} \right)_V = -S$$

$$F = U - TS$$

$$U = F + TS$$

Therefore:

$$U = F - T \left( \frac{\partial F}{\partial T} \right)_V$$

This is Gibbs-Helmholtz Equation.

The above equation is independent of Entropy, hence it can be easily applied to study the thermodynamics of isothermal changes in a chemical system.

### 3 Alternate derivation of Maxwell's Relations

The four Maxwell Relations can be derived in the following way. The state of a homogeneous system is determined completely if we know its mass and any two of the thermodynamic variables  $P, V, T, U$  and  $S$ . Thus the internal energy  $U$  of the system is completely determined if  $V$  and  $T$  are given. From the first law of thermodynamics, which gives us a differential form for the internal energy:

$$dU = dQ + dW$$

We know that the work done on a system,

$$dW = -PdV$$

Additionally, from the second law of thermodynamics, in terms of entropy, we know that the heat transferred is given by:

$$dQ = TdS$$

$$dU = TdS - PdV$$

Let us select  $x$  and  $y$  as any two independent variables out of the five ( $P, V, T, U, S$ ) Suppose  $U, S, V$  are functions of  $x$  and  $y$ . Therefore

$$\partial U = \left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy$$

$$\partial S = \left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy$$

$$\partial V = \left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{\partial y}\right)_x dy$$

Substituting values of  $dU, dS, dV$ ,

$$\left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy = T \left[ \left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy \right] - P \left[ \left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{\partial y}\right)_x dy \right]$$

Equating coefficients of  $dx, dy$ ,

$$\left(\frac{\partial U}{\partial x}\right)_y = T \left[ \left(\frac{\partial S}{\partial x}\right)_y \right] - P \left[ \left(\frac{\partial V}{\partial x}\right)_y \right]$$

$$\left(\frac{\partial U}{\partial y}\right)_x = T \left[ \left(\frac{\partial S}{\partial y}\right)_x \right] - P \left[ \left(\frac{\partial V}{\partial y}\right)_x \right]$$

Differentiating both the above equations by  $dy, dx$  respectively,

$$\left(\frac{\partial^2 U}{\partial x \partial y}\right) = \left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y + T \left(\frac{\partial^2 S}{\partial x \partial y}\right) - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y - P \left(\frac{\partial^2 V}{\partial x \partial y}\right)$$

$$\left(\frac{\partial^2 U}{\partial x \partial y}\right) = \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x + T \left(\frac{\partial^2 S}{\partial x \partial y}\right) - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x - P \left(\frac{\partial^2 V}{\partial x \partial y}\right)$$

Here  $dU$  is a perfect differential, and hence we can change the order of differentiation. Equating the above equations,

$$\left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y = \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x$$

This is the general Maxwell Equation. 1. First Relation

$x = S, y = V$

$$\frac{\partial S}{\partial x} = 1, \frac{\partial V}{\partial y} = 1$$

$$\frac{\partial S}{\partial y} = 0, \frac{\partial V}{\partial x} = 0$$

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

This is Maxwell's first thermodynamic relation.

1. First Relation

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2. Second Relation

$$x = T, y = V$$

$$\frac{\partial T}{\partial x} = 1, \frac{\partial V}{\partial y} = 1$$

$$\frac{\partial T}{\partial y} = 0, \frac{\partial V}{\partial x} = 0$$

$$0 = \left(\frac{\partial S}{\partial V}\right)_T - \left(\frac{\partial P}{\partial T}\right)_V$$

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

This is Maxwell's second thermodynamic relation.

3. Third Relation

$$x = S, y = P$$

$$\frac{\partial S}{\partial x} = 1, \frac{\partial P}{\partial y} = 1$$

$$\frac{\partial S}{\partial y} = 0, \frac{\partial P}{\partial x} = 0$$

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

This is Maxwell's third thermodynamic relation.

4. Fourth Relation

$$x = T, y = P$$

$$\frac{\partial T}{\partial x} = 1, \frac{\partial P}{\partial y} = 1$$

$$\frac{\partial T}{\partial y} = 0, \frac{\partial P}{\partial x} = 0$$

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

This is Maxwell's fourth thermodynamic relation.

## 4 Clausius Clayperon Equation

This relates the change in melting point and boiling point with change in pressure. The equation can be derived from Maxwells second thermodynamic relation

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

Multiplying both sides by T,

$$\begin{aligned} T \left(\frac{\partial P}{\partial T}\right)_V &= T \left(\frac{\partial S}{\partial V}\right)_T \\ &= \left(\frac{T\partial S}{\partial V}\right)_T \end{aligned}$$

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

Here  $\partial Q$  represents the heat absorbed at constant temperature, ie latent heat, Let unit mass of the substance under constant temperature get converted from one state to another absorbing an amount of heat  $L$ . Suppose the specific volumes in the first and second state are  $V_1$  and  $V_2$ , then  $\partial V = V_2 - V_1$ . Hence

$$T \left( \frac{\partial P}{\partial T} \right)_V = \left( \frac{L}{V_2 - V_1} \right)_T$$

$$T \left( \frac{\partial P}{\partial T} \right)_V = \frac{L}{V_2 - V_1}$$

$$\frac{\partial P}{\partial T} = \frac{L}{T(V_2 - V_1)}$$

This is Clausius Clayperon Equation.

Therefore, when  $V_2 > V_1$ , as for ice, gallium, the melting point increases with increase in pressure. When  $V_2 < V_1$ , as for wax and sulphur, the melting point decreases with increase in pressure.

## 5 Ratio of Specific Heats

The coefficient of volume elasticity is

$$E = \frac{\text{Stress}}{\text{Strain}} = -\frac{dP}{dV/V} = -V \frac{dP}{dV}$$

Therefore, the adiabatic elasticity  $E_S$  (entropy constant) and isothermal elasticity  $E_T$  (temperature constant) are:

$$E_S = -V \left( \frac{\partial P}{\partial V} \right)_S$$

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

Dividing the two equations:

$$\begin{aligned} \frac{E_S}{E_T} &= \frac{(\partial P/\partial V)_S}{(\partial P/\partial V)_T} \\ &= \frac{((\partial P/\partial T).(\partial T/\partial V))_S}{(\partial P/\partial S).(\partial S/\partial V)_T} \end{aligned}$$

Using Maxwell's relations

$$\begin{aligned} \frac{E_S}{E_T} &= \frac{(\partial S/\partial V)_P (\partial P/\partial S)_V}{(\partial T/\partial V)_P (\partial P/\partial T)_V} \\ &= \left( \frac{\partial S/\partial V}{\partial T/\partial V} \right)_P \left( \frac{\partial P/\partial S}{\partial P/\partial T} \right)_V \\ &= \left( \frac{\partial S}{\partial T} \right)_P \left( \frac{\partial T}{\partial S} \right)_V \end{aligned}$$

Multiplying the numerator and denominator by T,

$$\frac{E_S}{E_T} = \frac{T \left( \frac{\partial S}{\partial T} \right)_P}{T \left( \frac{\partial T}{\partial S} \right)_V} = \frac{\left( \frac{\partial Q}{\partial T} \right)_P}{\left( \frac{\partial Q}{\partial T} \right)_V}$$

But  $\left( \frac{\partial Q}{\partial T} \right)_P = C_P$  and  $\left( \frac{\partial Q}{\partial T} \right)_V = C_V$  Hence

$$\frac{C_P}{C_V} = \gamma = \frac{E_S}{E_T}$$

## 6 Difference of Specific Heats

$$\left(\frac{\partial Q}{\partial T}\right)_P = C_P \text{ and } \left(\frac{\partial Q}{\partial T}\right)_V = C_V$$

Therefore

$$\begin{aligned} C_P - C_V &= \left(\frac{\partial Q}{\partial T}\right)_P - \left(\frac{\partial Q}{\partial T}\right)_V \\ &= T \left(\frac{\partial S}{\partial T}\right)_P - T \left(\frac{\partial S}{\partial T}\right)_V \\ &= T \left[ \left(\frac{\partial S}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_V \right] \end{aligned}$$

Let Entropy be a function of V and T

$$S = f(V, T)$$

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

Therefore

$$C_P - C_V = T \left[ \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \right]$$

For a perfect gas

$$PV = RT$$

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

and

$$\left(\frac{\partial V}{\partial T}\right)_P = R/P$$

Substituting in the above equation,

$$C_P - C_V = T [R/V \times R/P] = TR^2/(PV) = R$$

$$C_P - C_V = R$$

## 7 Stefan Boltzmanns Law

The total radiant energy E emitted per second from unit surface area of a black body is proportional to the fourth power of its absolute temperature T.

$$E \propto T^4$$

$$E = \sigma T^4$$

where  $\sigma$  is Stefans constant. In SI units, its value is  $5.672 \times 10^{-8} J s^{-1} m^{-2} K^{-4}$  According to Maxwells Second Relation:

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

We know

$$dQ = dU + PdV$$

$$dQ = TdS$$

$$TdS = dU + PdV$$

$$dS = 1/T[dU + PdV]$$

Substituting above,

$$1/T \left[ \left( \frac{\partial U}{\partial V} \right)_T + P \right] = \left( \frac{\partial P}{\partial T} \right)_V$$

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

According to Maxwells electromagnetic theory, the black body radiation exerts a pressure P on the walls which is equal to  $u/3$

$$P = u/3$$

If V is the volume of the enclosure and u is the energy density then the total internal energy U is

$$U = uV$$

Substituting in above equation:

$$\left( \frac{\partial(uV)}{\partial V} \right)_T + \frac{u}{3} = \frac{T}{3} \left( \frac{\partial u}{\partial T} \right)_V$$

$$u + \frac{u}{3} = \frac{T}{3} \left( \frac{\partial u}{\partial T} \right)_V$$

$$\frac{4u}{3} = \frac{T}{3} \left( \frac{\partial u}{\partial T} \right)_V$$

$$\frac{du}{u} = 4 \frac{dT}{T}$$

$$\log u = 4 \log T + a$$

$$u = aT^4$$

The energy emitted per second per unit area is

$$E = \frac{1}{4}uc$$

where c is the velocity of light. Therefore

$$E = \frac{1}{4}aT^4c = \frac{1}{4}acT^4$$

$$E = \sigma T^4$$

## 8 Joule-Thomson or Joule- Kelvin effect

Joule-Thomson or Joule-Kelvin effect , the change in temperature that accompanies expansion of a gas without production of work or transfer of heat. At ordinary temperatures and pressures, all real gases except hydrogen and helium cool upon such expansion; this phenomenon often is utilized in liquefying gases. The phenomenon was investigated in 1852 by the British physicists James Prescott Joule and William Thomson (Lord Kelvin). The cooling occurs because work must be done to overcome the long-range attraction between the gas molecules as they move farther apart. Hydrogen and helium will cool upon expansion only if their initial temperatures are very low because the long-range forces in these gases are unusually weak.

We know

$$H = U + PV = \text{constant}$$

$$d(U + PV) = 0$$

$$dU + PdV + VdP = 0$$

from first and second law of thermodynamics

$$TdS = dU + PdV$$

$$TdS + VdP = 0$$



Let Entropy be a function of P and T

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

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

Substituting in above equation

$$T \left[ \left( \frac{\partial S}{\partial P} \right)_T dP + \left( \frac{\partial S}{\partial T} \right)_P dT \right] + V dP = 0$$

Now

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

and

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

Therefore

$$-T \left( \frac{\partial V}{\partial T} \right)_P dP + C_P dT + V dP = 0$$

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

$$C_P dT = \left[ T \left( \frac{\partial V}{\partial T} \right)_P - V \right] dP$$

$$\frac{dT}{dP} = \frac{1}{C_P} \left[ T \left( \frac{\partial V}{\partial T} \right)_P - V \right]$$

$$\left( \frac{dT}{dP} \right)_H = \frac{1}{C_P} \left[ T \left( \frac{\partial V}{\partial T} \right)_P - V \right]$$

If  $\left( \frac{\partial T}{\partial P} \right)_H$  is positive there is a heating effect If  $\left( \frac{\partial T}{\partial P} \right)_H$  is negative there is a cooling effect If  $\left( \frac{\partial T}{\partial P} \right)_H$  is positive there is neither cooling or heating effect

For a perfect gas

$$PV = RT$$

$$V = RT/P$$

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

Substituting

$$\left( \frac{dT}{dP} \right)_H = \frac{1}{C_P} \left[ T \left( \frac{R}{P} \right) - V \right] = 0$$

So Joule-Kelvin Effect for a perfect gas is zero.

## 9 Reversible Cell

A reversible cell is like a heat engine, where the cell is charged and discharged to get it back to its original condition.

Consider a reversible cell of emf  $E$  at temperature  $T_1$ . Let a charge  $q$  pass through it to charge it to an emf  $E$ . Lets say this cell does  $W$  amount of work and its emf drops from  $E$  to  $(E - dE)$  and temp from  $T$  to  $(T - dT)$ . Now a charge  $q$  is passed in the reverse direction and the cell comes back to its original condition.

This is exactly a Carnot Cycle with two adiabatic and two isothermal processes. Hence we apply the same formula as for Carnot engine. From second law of thermodynamics:

$$\frac{\text{Work done per cycle}}{\text{Heat absorbed}} = \frac{\text{Difference in temperature}}{\text{Temperature of the source}}$$

$$\frac{W}{Q} = \frac{(T_1 - T_2)}{T_1} = \frac{dT}{T}$$

Work done during charging =  $Eq$  Joules Let  $h$  be the energy drawn at high temperature.

$$\frac{W}{h} = \frac{dEq}{h} = \frac{dT}{T}$$

$$h = Tq \frac{dE}{dT}$$

The total energy provided by the cell is  $Eq$ .

$$Eq = h + Hq$$

$$Eq = Tq \frac{dE}{dT} + Hq$$

$$E = H + T \frac{dE}{dT}$$

This is Gibbs-Helmholtz Equation. If  $\frac{dE}{dT}$  is positive then emf rises with rise in temperature. If  $\frac{dE}{dT}$  is negative then emf falls with rise in temperature. If  $\frac{dE}{dT}$  is zero then no change in emf with temperature.