

Maxwell Relations

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$$G = Vdp - SdT + udn$$

$$\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y} \right) = \frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x} \right)$$

Thermodynamics

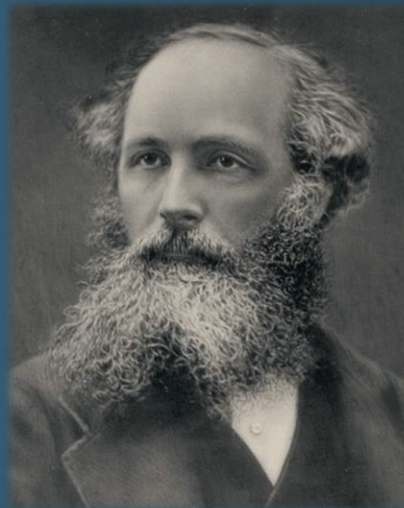
Dr. Hazem Falah Sakeek
Al-Azhar University - Gaza

Unit 5: Pure Substance

Lecture 28: Maxwell's Equations

Unit 5: Pure Substance

- Enthalpy
- The Helmholtz functions
- Gibbs functions
- Maxwell's Equations**
- The Tds equations
- Energy equations
- Heat-capacity equations



Example 1

One mole of ice is converted to water at 273 K in atmospheric pressure, the change in volume is $1.64 \times 10^{-6} \text{ m}^3$. If the latent heat of fusion is 6030 J/mole, **calculate the change in internal energy, change in entropy, change in Gibb's function.**

(i) The change in internal energy $\Delta U = Q + W$

$$\Delta U = Q + P\Delta V = 6030 + 1 \times 10^5(1.6 \times 10^{-6}) = 6030.16 \text{ J}$$

(ii) The change in entropy $\Delta S = \frac{\Delta Q}{T}$

$$= \frac{6030}{273} = 22 \text{ J/K}$$

(iii) The change in Gibb's function $\Delta G = V\Delta P - S\Delta T = 0$

Since $\Delta P = 0$ (isobaric process) and $\Delta t = 0$ (isothermal process)

Example 2

Prove that the change in pressure with respect to the temperature in phase change is given by

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

For phase change $dG = 0$

Therefore, $G = \text{constant}$

Then,

$$g' = g'' \text{ for fusion curve}$$

$$g'' = g''' \text{ for vaporization curve}$$

$$g' = g''' \text{ for sublimation curve}$$

Where g' for gas phase, g'' for liquid phase, g''' for solid phase

$$dG = VdP - SdT$$

عند زيادة درجة الحرارة من T إلى $T + dT$ فإن الضغط يزداد من P إلى $P + dP$ وكذلك تزداد دالة جيبس من g' إلى $g' + dg'$ ومن g'' إلى $g'' + dg''$

ولكن في حالة الاتزان يكون التغير في دالة جيبس ثابتا اي ان

$$g' = g''$$

$$g' + dg' = g'' + dg''$$

$$dg' = dg''$$

$$dg' = V_1 dP - S_1 dT$$

$$dg'' = V_2 dP - S_2 dT$$

معادلة كلاوزيوس-كلايرون
Clausius–Clapeyron relation

ما هو الضغط اللازم لانصهار الثلج عند درجة حرارة أقل بمقدار ΔT من الصفر المتوي؟

بمساواة المعادلتين نحصل على ما يلي:

$$(V_2 - V_1) dP = (S_2 - S_1) dT$$

$$\frac{dP}{dT} = \frac{\Delta S}{(V_f - V_i)} = \frac{L}{T(V_f - V_i)}$$

Maxwell's Equations

A set of equations in thermodynamics which are derivable from the symmetry of second derivatives and from the definitions of the thermodynamic potentials. These relations are named for the nineteenth-century physicist James Clerk Maxwell.

Theorem: Condition for an exact differential

If a relation exists among x , y , and z , we may imagine z expressed as a function of x and y ; hence,

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

If we let

$$M = \left(\frac{\partial z}{\partial x}\right)_y \quad \text{and} \quad N = \left(\frac{\partial z}{\partial y}\right)_x$$

then

$$dz = Mdx + Ndy$$

where z , M , and N are all functions of x and y .

Partially differentiating M with respect to y , and N with respect to x , we get

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial^2 z}{\partial y \partial x}\right) \quad \text{and} \quad \left(\frac{\partial N}{\partial x}\right)_y = \left(\frac{\partial^2 z}{\partial y \partial x}\right)$$

Since the two second derivatives of the right-hand terms are equal, it follows that

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

This is known as the condition for an exact differential.

Maxwell's Equations

The properties of a pure substance are conveniently represented in terms of these four functions

Internal Energy	• U
Enthalpy	• $H = U + PV$
Helmholtz Function	• $F = U - TS$
Gibbs Function	• $G = H - TS$

Any one of these may be regarded as a function of any two of P , V , and T .

Suppose for example that both U and S are expressed as functions of V and T , thus

$$U = \text{function of } (V, T) \quad \text{and} \quad S = \text{function of } (V, T)$$

The second equation $S = \text{function of } (V, T)$ may be imagined to be solved for T in terms of S and V ;

Substituting this value of T in the first equation $U = \text{function of } (V, T)$, we should then have

$$U = \text{function of } (S, V)$$

Now imagine a hydrostatic system undergoing an infinitesimal reversible process from one equilibrium state to another

1 The internal energy changes by an amount

$$dU = TdS - PdV$$

2 The enthalpy changes by an amount

$$dH = TdS + VdP$$

3 The Helmholtz function changes by an amount

$$dF = -SdT - PdV$$

4 The Gibbs function changes by an amount

$$dG = -SdT + VdP$$

Since U , H , F , and G are actual functions, their differentials are exact differentials of the type

$$dz = Mdx + Ndy$$

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

Maxwell's equations

Applying this result to the four exact differentials dU , dH , dF , and dG :

$$dz = Mdx + Ndy$$

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

1	$dU = TdS - PdV$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$
2	$dH = TdS + VdP$	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$
3	$dF = -SdT - PdV$	$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$
4	$dG = -SdT + VdP$	$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

Maxwell's equations are extremely useful, because they provide relationships between measurable quantities and those which either cannot be measured or are difficult to measure.

إلى اللقاء مع المحاضرة (٢٩)

The Tds equations