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Thermodynamics (2) MPEG 122

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Thermodynamic Relations

Chapter Contents

The objective of the present chapter is to study Ideal and Real Gases, includes;

- Introduction.
- Fundamental of Partial Differentiation.
- Helmholtz and Gibbs Functions.
- Some General Thermodynamic Relations.
- Internal Energy and Enthalpy of a Perfect Gas.
- Property Relation from Exact Differentials.
- Maxwell Relations.
- Entropy Equations (T.ds Equations).
- Equations for Internal Energy and Enthalpy.
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- Joule-Thomson Coefficient.
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Introduction

- Eight properties of a system, p, T, v, u, h, s, Helmholtz function (f) and Gibbs function (g)
- h, f and g are sometimes referred to as thermodynamic potentials.
- h, f, and g are combinations of properties.
- Both f and g are useful when considering chemical reactions, and the former is of fundamental importance in statistical thermodynamics.
- The g is also useful when considering processes involving a change of phase.
- Only the first three, i.e., p, v and T are directly measurable.
- Combinations of properties might be called 'thermodynamic gradients'; they are all defined as the rate of change of one property with another while a third is kept constant.

Fundamental of Partial Differentiation

Fundamental of Partial Differentiation

$$f(x, y, z) = 0$$

$$x = x(y, z) \qquad \& \quad y = y(x, z) \qquad \& \qquad z = z(x, y)$$

- Let x is a function of two independent variables y and z;

$$x = x(y, z)$$

- Then the exact differential is dx;

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

$$let \qquad \left(\frac{\partial x}{\partial y}\right)_z = M \qquad \& \qquad \left(\frac{\partial x}{\partial z}\right)_y = N$$

$$then \qquad dx = Mdy + Ndz$$

- Partial differentiation of M and N with respect to z and y, respectively, gives;

$$\frac{\partial M}{\partial z} = \frac{\partial^2 x}{\partial y \partial z} \qquad and \qquad \frac{\partial N}{\partial y} = \frac{\partial^2 x}{\partial z \partial y}$$

$$\frac{\partial M}{\partial z} = \frac{\partial N}{\partial y} \dots \dots \dots \dots \dots . (i)$$

- dx is a perfect differential when eqn. (i) is satisfied for any function x. Similarly if;

$$y = y(x, z) \qquad \& \qquad z = z(x, y)$$

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

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

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

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

$$d\cancel{y} = \left[\left(\frac{\partial y}{\partial x}\right)_z + \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y\right] dx + \cancel{dy}$$

$$\left(\frac{\partial y}{\partial x}\right)_z + \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = 0$$

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

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

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{-1}{\left(\frac{\partial y}{\partial x}\right)_z}$$

- This known as reciprocity relation.
- In terms of p, v and T, the following relation holds well;

$$f(x, y, z) = f(p, v, T)$$

$$\left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_v = -1$$

$$W = Q - (u_0 - u_1)$$
$$W = T.ds - (u_0 - u_1)$$
$$W = T.(s_0 - s_1) - (u_0 - u_1)$$
$$W = (u_1 - T.s_1) - (u_0 - T.s_0) = f_1 - f_0$$

- The term (u – T.s) is known as **Helmholtz function** (*f*).
- This gives maximum possible output when the heat Q is transferred at constant temperature.
- If work against atmosphere is equal to $p_0(v_0 - v_1)$, then the maximum work available,

$$W_{max} = W - work\ against\ atmosphere$$
$$W_{max} = W - p_0(v_0 - v_1) = (u_1 - T.s_1) - (u_0 - T.s_0) - p_0(v_0 - v_1)$$
$$W_{max} = (u_1 + p_0.v_1 - T.s_1) - (u_0 + p_0.v_0 - T.s_0)$$
$$W_{max} = (h_1 - T.s_1) - (h_0 - T.s_0)$$
$$W_{max} = g_1 - g_0$$

- Where (h – T.s) is known as **Gibb's function or free energy function** (*g*).

Some General Thermodynamic Relations

- The first law applied to a closed system undergoing a reversible process states that;

$$dQ = du + p.dv$$

- According to second law;

$$ds = \left(\frac{dQ}{T}\right)_{rev.} \rightarrow T.ds = dQ$$

- Combining these equations, we get;

$$T.ds = du + p.dv$$

$$du = T.ds - p.dv$$

- The properties h, f and g may also be put in terms of T, s, p and v as follows:
- The enthalpy can be written as;

$du = T.ds - p.dv$

$$h = u + pv \;\rightarrow\; dh = du + p.dv + v.dp \;\rightarrow\; dh = (T.ds - p.dv) + p.dv + v.dp$$

$$\boldsymbol{dh = T.ds + v.dp}$$

- Helmholtz free energy function (f);

$du = T.ds - p.dv$

$$f = u - T.s$$

$$df = du - s.dT - T.ds = (T.ds - p.dv) - s.dT - T.ds$$

$$\boldsymbol{df = -p.dv - s.dT}$$

- Gibb's free energy function (g);

$dh = T.ds + v.dp$

$$g = h - T.s$$

$$dg = dh - T.ds - s.dT$$

$$dg = T.ds + v.dp - T.ds - s.dT$$

$$dg = v.dp - s.dT$$

- The principal results of this section are obtained;

$$du = Tds - pdv$$

$$dh = Tds + vdp$$

$$df = -pdv - sdT$$

$$dg = vdp - sdT$$

- For present purposes, it is convenient to express them as;

$$x = x(y,z) \qquad and \qquad dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz = Mdy + Ndz$$

$\boldsymbol{u = u(s, v)}$

$$du = T.ds - p.dv$$

$$du = \left(\frac{\partial u}{\partial s}\right)_v ds + \left(\frac{\partial u}{\partial v}\right)_s dv$$

$$T = \left(\frac{\partial u}{\partial s}\right)_v$$

$$-p = \left(\frac{\partial u}{\partial v}\right)_s$$

$\boldsymbol{h = h(s, p)}$

$$dh = T.ds + v.dp$$

$$dh = \left(\frac{\partial h}{\partial s}\right)_p ds + \left(\frac{\partial h}{\partial p}\right)_s dp$$

$$T = \left(\frac{\partial h}{\partial s}\right)_p$$

$$v = \left(\frac{\partial h}{\partial p}\right)_s$$

$\boldsymbol{f = f(v, T)}$

$$df = -p.dv - s.dT$$

$$df = \left(\frac{\partial f}{\partial v}\right)_T dv + \left(\frac{\partial f}{\partial p}\right)_v dT$$

$$-p = \left(\frac{\partial f}{\partial v}\right)_T$$

$$-s = \left(\frac{\partial f}{\partial p}\right)_v$$

$\boldsymbol{g = g(p, T)}$

$$dg = v.dp - s.dT$$

$$dg = \left(\frac{\partial g}{\partial p}\right)_T dp + \left(\frac{\partial g}{\partial T}\right)_p dT$$

$$v = \left(\frac{\partial g}{\partial p}\right)_T$$

$$-s = \left(\frac{\partial g}{\partial T}\right)_p$$

$$\left(\frac{\partial u}{\partial s}\right)_v = \left(\frac{\partial h}{\partial s}\right)_p = T$$

$$\left(\frac{\partial u}{\partial v}\right)_s = \left(\frac{\partial f}{\partial v}\right)_T = -p$$

$$\left(\frac{\partial h}{\partial p}\right)_s = \left(\frac{\partial g}{\partial p}\right)_T = v$$

$$\left(\frac{\partial f}{\partial p}\right)_v = \left(\frac{\partial g}{\partial T}\right)_p = -s$$

- The complete group of such relations may be summarized as follows:

$$\left(\frac{\partial u}{\partial s}\right)_v = \left(\frac{\partial h}{\partial s}\right)_p = T$$

$$\left(\frac{\partial u}{\partial v}\right)_s = \left(\frac{\partial f}{\partial v}\right)_T = -p$$

$$\left(\frac{\partial h}{\partial p}\right)_s = \left(\frac{\partial g}{\partial p}\right)_T = v$$

$$\left(\frac{\partial f}{\partial p}\right)_v = \left(\frac{\partial g}{\partial T}\right)_p = -s$$

- Let z is a function of two independent variables x and y;

$$z = z(x, y)$$

- Then the exact differential is dz;

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

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

$$dx = Mdx + Ndy$$

- Partial differentiation of M and N with respect to z and y, respectively, gives;

$$\frac{\partial}{\partial y}\left[\left(\frac{\partial z}{\partial x}\right)_y\right]_x = \frac{\partial}{\partial x}\left[\left(\frac{\partial z}{\partial y}\right)_x\right]_y$$

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

$$u = u(s, v)$$

$$du = T.ds - p.dv \qquad du = \left(\frac{\partial u}{\partial s}\right)_v ds + \left(\frac{\partial u}{\partial v}\right)_s dv$$

$$T = \left(\frac{\partial u}{\partial s}\right)_v \quad and \quad -p = \left(\frac{\partial u}{\partial v}\right)_s$$

- So;

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v \dots\dots\dots\dots\dots\dots (i)$$

$$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_p \dots\dots\dots\dots\dots\dots (ii)$$

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T \dots\dots\dots\dots\dots\dots (iii)$$

$$\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T \dots\dots\dots\dots\dots\dots (v)$$

The equations (i) to (v) are known as Maxwell relations.

Entropy Equations (T.ds Equations)

$$s = s(T, v)$$

$$ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv$$

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T$$

$$T.ds = T\left(\frac{\partial s}{\partial T}\right)_v dT + T\left(\frac{\partial s}{\partial v}\right)_T dv$$

- But for a reversible constant volume change;

$$dQ = c_v.(dT)_v$$

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

$$T.ds = c_v.dT + T\left(\frac{\partial p}{\partial T}\right)_v dv$$

- This is known as the first form of entropy equation or the first T.ds equation

$$s = s(T,p)$$

$$ds = \left(\frac{\partial s}{\partial T}\right)_p dT + \left(\frac{\partial s}{\partial p}\right)_T dp$$

$$\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T$$

$$T.ds = T\left(\frac{\partial s}{\partial T}\right)_p dT + T\left(\frac{\partial s}{\partial p}\right)_T dp$$

- But for a reversible constant pressure change;

$$dQ = c_p.(dT)_p = T.(ds)_p$$

$$c_p = T.\left(\frac{\partial s}{\partial T}\right)_p$$

So;

$$Tds = c_p.dT - T\left(\frac{\partial v}{\partial T}\right)_p dp$$

- This is known as the second form of entropy equation or the second T.ds equation.

The End of Lecture