2 PARTIAL DIFFERENTIALS.

As we have already seen, only two variables in a function of state are independent and any other variable (the state function) may be expressed in terms of the two independent ones (called state variables).

We have found the equation of state for an ideal gas previously;

$$PV = nRT$$

$$PV = \frac{2}{3}U$$

There is another equation of state frequently used for non-ideal gases, the Van der Waals equation

$$\left(P + \frac{n^2 a^2}{V^2}\right) \left(\frac{V}{n} - b\right) = RT$$

$$U = \frac{3}{2}nRT - \frac{n^2a}{V}$$

These equations of state all take a general mathematical form

$$PV - nRT = 0$$

Or

$$f(P,V,T) = 0$$

Similarly with the other equation of state

$$PV - \frac{2}{3}U = 0$$

or

$$f(P,V,U) = 0$$

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In general when we have a function of state f(x, y, z) = 0 and this has consequences

(i) <u>An Analytic Meaning.</u> Any one variable can be found as a function of the other two which may then be regarded as independent

Example. $f(x, y, z) = z^4 - x^2 - y^2 = 0$

$$z = \sqrt[4]{x^2 + y^2} = z(x, y)$$
$$x = \sqrt{z^4 - y^2} = x(y, z)$$
$$y = \sqrt{z^4 - x^2} = y(x, z)$$

(ii) <u>A geometric Meaning.</u> The equation of state defines a surface in x, y, z space



An equilibrium state can be thought of as a unique point on such a surface. In thermodynamics we are concerned with the changes from one equilibrium state to another known as a **process**. This change proceeds along the surface if there are no departures from equilibrium during the process, ie. if the final equilibrium state is reached via a series of intermediate equilibrium states the change is said to have been

carried out quasi-statically. On the other hand if the change is made rapidly there will be excursions into non-equilibrium states.



In the diagram above a "process" is shown where the gas is expanded in going from A to B and this is shown on the *PVT* diagram in a non-isothermal process ie. we can see that the temperature changes going from A to B, it is reduced.

With two independent variables where we need to describe changes we need to use partial differentation as is clear by study of the above diagrams.

Going from one position on the surface to an infinitesimally close position (equilibrium state) we need to find how the dependent variable changes as we change first one of the independent variables and then the other whilst the partner remains fixed. Ie. if z is the dependent variable and z = z(x,y), we need to know how z changes with x while y is

held fixed, $\left(\frac{\partial z}{\partial x}\right)_y$ and how z changes with y whilst x is held fixed, $\left(\frac{\partial z}{\partial y}\right)_x$

$$x_B = x_A + \mathrm{d}x \qquad \qquad y_B = y_A + \mathrm{d}y$$

$$dz = z(x_B, y_B) - z(x_A, y_A) = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$
(1.1a)

We could also have used *y* as the dependent variable, y = y(x,z)

$$dy = y(x_B, z_B) - z(x_A, z_A) = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz$$
(1.1b)

Or we could use *x* as the dependent variable, x = x(y,z)

$$dx = x(z_B, y_B) - x(z_A, y_A) = \left(\frac{\partial x}{\partial z}\right)_y dz + \left(\frac{\partial x}{\partial y}\right)_z dy$$
(1.1c)

In all three equations 1.1 dx, dy and dz are identical which implies that there are relationships amongst the partial differentials which can be discovered.

The first of these are **<u>the reciprocal relations</u>** found as follows;

If we choose dy = 0.

From 1.1a
$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx$$
 (1.2a)

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And from 1.1c
$$dx = \left(\frac{\partial x}{\partial z}\right)_y dz$$
 (1.2b)

From equations 1.2

$$\left(\frac{\partial z}{\partial x}\right)_{y} = \frac{1}{\left(\frac{\partial x}{\partial z}\right)_{y}}$$
(1.3a)

Similarly we make dx = 0 to find

$$\left(\frac{\partial z}{\partial y}\right)_{x} = \frac{1}{\left(\frac{\partial y}{\partial z}\right)_{x}}$$
(1.3b)

and for dz = 0 we have

$$\left(\frac{\partial y}{\partial x}\right)_{z} = \frac{1}{\left(\frac{\partial x}{\partial y}\right)_{z}}$$
(1.3c)

Equations 1.3 are called THE RECIPROCAL RELATIONS.

We may now find the second of these relationships, <u>the cyclical relations</u>, as follows;

We may substitute 1.1c into 1.1a to find

$$dz = \left(\frac{\partial z}{\partial x}\right)_{y} \left[\left(\frac{\partial x}{\partial y}\right)_{z} dy + \left(\frac{\partial x}{\partial z}\right)_{y} dz\right] + \left(\frac{\partial z}{\partial y}\right) dy$$
(1.4)

By expanding and then using the reciprocal relations 1.4 becomes

$$dz = \left[\left(\frac{\partial z}{\partial x} \right)_{y} \left(\frac{\partial x}{\partial y} \right)_{z} + \left(\frac{\partial z}{\partial y} \right)_{x} \right] dy + \left(\frac{\partial z}{\partial x} \right)_{y} \left(\frac{\partial x}{\partial z} \right)_{z} dz$$
(1.5a)

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$$dz = \left[\left(\frac{\partial z}{\partial x} \right)_{y} \left(\frac{\partial x}{\partial y} \right)_{z} + \left(\frac{\partial z}{\partial y} \right)_{x} \right] dy + dz$$
(1.5b)

$$\left(\frac{\partial z}{\partial x}\right)_{y}\left(\frac{\partial x}{\partial y}\right)_{z} = -\left(\frac{\partial z}{\partial y}\right)_{x} = \frac{-1}{\left(\frac{\partial y}{\partial z}\right)_{x}}$$
(1.5c)

And finally

$$\left(\frac{\partial z}{\partial x}\right)_{y} \left(\frac{\partial x}{\partial y}\right)_{z} \left(\frac{\partial y}{\partial z}\right)_{x} = -1$$
(1.6)

Equation 1.6 is called the CYCLICAL RELATION

An easy way to remember this equation is to take the following row of variables



We frequently use partial differentials to define important properties of a thermodynamic system.

Ideal gas equation of state. Example

$$PV = RT$$

The three variables are P,V,T and we form the cyclic relation in the way shown above

$$P \qquad V \qquad T \qquad P \qquad T \qquad P \qquad T = -1$$

$$P = \frac{RT}{V} \qquad V = \frac{RT}{P} \qquad T = \frac{PV}{R}$$

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$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{-RT}{V^2} \qquad \qquad \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} \qquad \qquad \left(\frac{\partial T}{\partial P}\right)_V = \frac{V}{R}$$

$$\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = \frac{-RT}{V^2} \frac{R}{P} \frac{V}{R} = \frac{-PV}{V^2} \frac{R}{P} \frac{V}{R} = -1 \qquad (\text{QED})$$

Example. Coefficient of thermal expansion is defined for a fluid as

$$\frac{Fractional \ Volume \ Change}{Temperature \ Change} = \beta = \frac{1}{\Delta T} \frac{\Delta V}{V}$$

Or more precisely in terms of partial differentials

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{P} \tag{1.7}$$

Here P, V and T are the variables and as V depends on T because of the partial differential T and P are the two independent variables or state variables and V the state function.

Example. (Isothermal) Bulk Modulus is defined for a fluid as

$$\frac{Change \text{ in } \mathbf{Pr} \text{ essure}}{-Fractional Volume Change} = \kappa = -\frac{V}{\Delta V} \Delta P$$

NB the negative sign in the definition of κ ensures that κ has a positive value.

Again we need to write this using partial differentials noting that we need the isothermal form ie. temperature is held constant.

$$\kappa = -V \left(\frac{\partial P}{\partial V}\right)_T \tag{1.8}$$

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Looking at 1.8 we note that P depends on V and is therefore a dependent variable leaving V and T as the two independent variables or state variables and P is the state function.

We can see by combining 1.7 and 1.8

$$K\beta = -\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{\left(\frac{\partial T}{\partial P}\right)_V} = \left(\frac{\partial P}{\partial T}\right)_V$$
(1.9)

Where the cyclical and reciprocal relations were used in steps 2 and 3 of 1.9 to remove the minus sign and then to obtain a more direct final result.