Definition of β

- Volume expansivity β is a measureable quantity, and from it we can determine via its relationship to the changes of thermodynamic coordinates V and T

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

- It is normally a positive number since most substance expand when its temperature rises

Definition of κ

- Isothermal compressibility κ is a measureable quantity, and from it we can determine via its relationship to the changes of thermodynamic coordinates *V* and *P*

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

- These are usually positive numbers

Relating partial derivatives with experimental measurements

- κ and β are experimental quantities
- The partial derivatives of the thermo coordinates are theoretical construct
- Measuring κ and β allows us to gain information on the equation of states in terms of the partial derivatives of the thermo coordinates.

Mathematical theorems in partial differential calculus

- Consider an EoS. This is in general an equation that relates the thermodynamical coordinates, say, x, y, z. (Think of P,V,T)
- The general form of an EoS is $f(x, y, z) = 0$.
- The EoS serves to constrain the relation of how x, y, z can vary
- Hence, in general, any one of the thermodynamical coordinates can be expressed as a function of each another, e.g. $x=x(y,z)$

Mathematical theorems in partial differential calculus

- Since x=x(y,z), the differential of x, according to calculus, is

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

- So is

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

- Combining both equation, we have

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

- If dz = 0 and dx ≠ 0, then

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

- dx and dz are two independent variables
- If dx = 0, and dz ≠ 0, then

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

- Combining both,

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

Q1) Find β/κ for an ideal gas?

Q2) Prove chain rule for an ideal gas?

Solution of Question1

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

From ideal gas equation of state

Pv=RT $\Rightarrow$ $v = \frac{RT}{P}$ $\Rightarrow$

by differentiation we get $\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{P}$

Substituting this eq. in eq.(1) we get:

$\beta = \frac{1}{T}$ - - - - - - - - - (2)

Also we have K=- $\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$ - - - - - - - (3)

From ideal gas equation of state

Pv=RT $\Rightarrow$ $v=\frac{RT}{P}$ $\Rightarrow$

by differentiation we get $\left(\frac{\partial v}{\partial P}\right)_T=-\frac{RT}{P^2}$

Substituting this eq. in eq.(3) we get:

K= $\frac{1}{P}$ - - - - - - - - (4)

Now for question (1) we divide equation (2) over equation **(4)** to get:

$$\frac{\beta}{K}=\frac{P}{T}$$

Solution of Question2

The chain rule in thermodynamics can be concluded when Identifying $x = P$, $y = V$, $z = T$, so that

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \rightarrow \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1 \quad \text{---------} \; (1)$$

Now from the ideal gas EOS we can deduce that:

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{V^2} \quad \text{------} \; (2)$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} \quad \text{--------} \; (3)$$

$$\left(\frac{\partial T}{\partial P}\right)_V = \frac{V}{R} \quad \text{--------} \; (4)$$

Putting (2), (3) and (4) in (1) we get

LHS = RHS = -1