### Science-1

# Assignment-3

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### Question 1

For plot (i), y = x for  $0 \le x \le 1, 0 \le y \le 1$ 

For plot (ii), y = 0 for  $0 \le x < 1$  and x = 1 for  $0 < y \le 1$ 

$$df = d(xy)$$
$$df = (dx)y + x(dy)$$

$$df = xdx + ydy$$

$$\int df = \int_0^1 xdx + \int_0^1 ydy$$

$$\int df = \left[\frac{x^2}{2}\right]_0^1 + \left[\frac{y^2}{2}\right]_0^1$$

$$\int df = \frac{1}{2} + \frac{1}{2}$$

$$\int df = 1$$

$$\int df = \int_0^1 x dx + \int_0^0 y dy + \int_1^1 x dx + \int_0^1 y dy$$

$$\int df = \left[\frac{x^2}{2}\right]_0^1 + 0 + 0 + \left[\frac{y^2}{2}\right]_0^1$$

$$\int df = \frac{1}{2} + \frac{1}{2}$$

$$\int df = 1$$

(b)

$$df = d(xy)$$

Note that the integral is path independent.

Since df is equal to the differential of a differentiable function xy, it is an exact differential.

(c)

$$dg = ydx$$

$$dg = xdx$$

$$\int dg = \int_0^1 xdx$$

$$\int dg = \left[\frac{x^2}{2}\right]_0^1$$

$$\int dg = \frac{1}{2}$$

(ii)

$$dg = ydx$$

$$\int dg = \int_0^1 0dx + \int_1^1 1dx$$

$$\int dg = 0$$

(d)

$$dg = ydx$$

Note that the integral is path dependent

Since dg is not equal to the differential of a differentiable function, it is an inexact differential.

### Question 2

Assuming 1 mole of gas as  $U = C_V T$ 

Let  $\rho$  be the mass density, p be the pressure, V be the volume, M be the molar mass.

We know that  $C_v = \frac{R}{1-\gamma}$ , where R is the gas constant.

(i)

$$U=C_VT$$

$$\frac{U}{M} = \frac{C_V T}{M}$$

Since pV = RT

$$\frac{U}{M} = \frac{C_V p V}{M R}$$

Since  $\rho = \frac{M}{V}$ 

$$\frac{U}{M} = \frac{C_V p}{\rho R}$$

$$\frac{U}{M} = \frac{\textit{Rp}}{\rho \textit{R}(\gamma - 1)}$$

$$\frac{U}{M} = \frac{p}{\rho(\gamma - 1)}$$

This is the required internal energy per unit mass.

(ii)

$$U = \frac{RT}{\gamma - 1}$$

$$\frac{U}{V} = \frac{RT}{V(\gamma-1)}$$

Since pV = RT

$$\frac{U}{V} = \frac{p \mathcal{V}}{\mathcal{V}(\gamma - 1)}$$

$$\frac{U}{V} = \frac{p}{\gamma - 1}$$

This is the required internal energy per unit volume.

#### **Question 3**

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p$$

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

For a van der Waals gas,

$$\begin{split} RT &= \bigg(p + \frac{a}{V^2}\bigg)(V-b) \\ R\bigg(\frac{\partial T}{\partial V}\bigg)_p &= \bigg(p + \frac{a}{V^2}\bigg) - \frac{2a}{V^3}(V-b) \\ \bigg(\frac{\partial V}{\partial T}\bigg)_p &= \frac{RV^3}{V(pV^2+a) - 2a(V-b)} \\ \alpha &= \frac{RV^2}{V(pV^2+a) - 2a(V-b)} \end{split}$$

This is the coefficient of thermal expansion  $\alpha$  for a van der Waals gas.

Now, for isothermal compressibility:

$$\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T$$

At a constant temperature, on increasing the pressure, the volume of a gas decreases. This will result in  $\left(\frac{\partial V}{\partial p}\right)_T$  being negative. Hence, for the constant  $\kappa_T$  to be positive, the RHS is multiplied by -1.

Now, to prove the required relation:

$$\begin{split} \left(\frac{\partial V}{\partial p}\right)_T &= \frac{1}{\left(\frac{\partial p}{\partial V}\right)_T} \\ p &= \frac{RT}{V-b} - \frac{a}{V^2} \\ \left(\frac{\partial p}{\partial V}\right)_T &= -\frac{RT}{\left(V-b\right)^2} + \frac{2a}{V^3} \end{split}$$

On substituting RT from the van der Waals gas equation,

$$\left(\frac{\partial p}{\partial V}\right)_T = -\left(p + \frac{a}{V^2}\right) \frac{\cancel{V-b}}{(V-b)^2} + \frac{2a}{V^3}$$

$$\left(\frac{\partial V}{\partial p}\right)_T = \frac{V^3(V-b)}{2a(V-b) - V(pV^2 + a)}$$

$$\kappa_T = \frac{V^2(V-b)}{V(pV^2 + a) - 2a(V-b)}$$

$$\kappa_T R = \frac{RV^2}{V(pV^2 + a) - 2a(V-b)}(V-b)$$

$$\kappa_T R = \alpha(V-b)$$

For one mole of gas,  $V=V_m$ 

$$\kappa_T R = \alpha (V_m - b)$$

Hence, proven.

## Question 4

Assuming n moles of liquid water initially at  $-10^{\circ}C$ .

Let the latent heat of fusion of water be L, specific heat of water be s.

Since result is a mixture of ice and water, this is only possible at tempetarure  $T_2=0^oC$ .  $(T_1=-10^oC)$ 

Therefore,  $\Delta T = 10K$ .

Since the compartment is thermally insulated, q=0J.

The latent heat of ice will be compensted by the heating of water.

$$n*18*s*\Delta T = m_{\rm ice}*L$$
 
$$m_{\rm ice} = \frac{18ns\Delta T}{L}$$

Let  ${\cal H}_1$  be enthalpy change in heating of water and  ${\cal H}_2$  be enthalpy change of fusion.

$$\begin{split} \Delta H &= \Delta H_1 + \Delta H_2 \\ \Delta H_1 &= 18 n s \Delta T \\ \Delta H_2 &= \Delta H_{\mathrm{fusion}} = -m_{\mathrm{ice}} L \\ \Delta H &= 18 n s \Delta T - m_{\mathrm{ice}} L \\ \Delta H &= 0 \end{split}$$

Note that for liquids and solids,  $\Delta U \approx \Delta H$ 

$$\Delta U = 0$$

From first law of thermodynamics

$$\Delta U = q + w$$
$$w = 0$$

Let  $\Delta S_1$  be entropy change in heating of water and  $\Delta S_2$  be entropy change of fusion.

$$\begin{split} \Delta S_1 &= ms \ln \left(\frac{T_2}{T_1}\right) \\ \Delta S_1 &= 18ns \ln \left(\frac{283}{273}\right) \\ \Delta S_2 &= \frac{\Delta H_{\text{fusion}}}{T} \\ \Delta S_2 &= -\frac{m_{\text{ice}}L}{273} \\ \Delta S_2 &= -\frac{18ns\Delta T}{273} \\ \Delta S_2 &= -\frac{60ns}{91} \\ \Delta S &= ns \left(18 \ln \left(\frac{283}{273}\right) - \frac{60}{91}\right) \end{split}$$