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.

(e)

g should be called a path function and f should be called a state function. $\int dg$ is an inexact differential and depends on the path, hence it as a path function. $\int df$ is an exact differential and is independent of the path taken, hence it is a state function.

Question 2

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

Let ρ 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

$$\frac{U}{M} = \frac{C_V pV}{MR}$$

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

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

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

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

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 α for a van der Waals gas.

Now, for isothermal compressibility:

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

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 κ_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,

$$\begin{split} \left(\frac{\partial p}{\partial V}\right)_T &= -\left(p + \frac{a}{V^2}\right) \frac{\mathcal{V} - \mathcal{b}}{(V - b)^2} + \frac{2a}{V^3} \\ \left(\frac{\partial V}{\partial p}\right)_T &= \frac{V^3(V - b)}{2a(V - b) - V(pV^2 + a)} \\ \kappa_T &= \frac{V^2(V - b)}{V(pV^2 + a) - 2a(V - b)} \\ \kappa_T R &= \frac{RV^2}{V(pV^2 + a) - 2a(V - b)} (V - b) \\ \kappa_T R &= \alpha(V - b) \end{split}$$

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 ΔS_1 be entropy change in heating of water and ΔS_2 be entropy change of fusion.

$$\begin{split} \Delta S_1 &= m s \ln \left(\frac{T_2}{T_1}\right) \\ \Delta S_1 &= 18 n s \ln \left(\frac{273}{263}\right) \\ \Delta S_2 &= \frac{\Delta H_{\text{fusion}}}{T} \\ \Delta S_2 &= -\frac{m_{\text{ice}} L}{273} \\ \Delta S_2 &= -\frac{18 n s \Delta T}{273} \\ \Delta S_2 &= -\frac{60 n s}{91} \\ \Delta S &= n s \left(18 \ln \left(\frac{273}{263}\right) - \frac{60}{91}\right) \end{split}$$