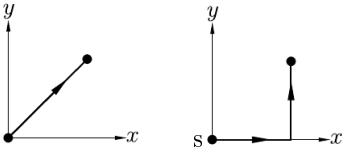


1. Consider the processes $(x, y) : (0, 0) \rightarrow (1, 1)$ shown in the following plots :



- (a) Calculate the change in the function $f(x, y) = xy$ for the two processes by integrating df over the paths shown.

Ans. $df = d(xy) = ydx + xdy$

First process : $x = y \Rightarrow \Delta f = \int_{(0,0)}^{(1,1)} df = \int_{(0,0)}^{(1,1)} ydx + \int_{(0,0)}^{(1,1)} xdy = 2 \int_0^1 ydy = 2 \cdot \frac{y^2}{2} \Big|_0^1 = 1$

Second process : $\Delta f = \int_{(0,0)}^{(1,1)} df = \int_{(0,0)}^{(1,0)} ydx + \int_{(0,0)}^{(1,0)} xdy + \int_{(1,0)}^{(1,1)} ydx + \int_{(1,0)}^{(1,1)} xdy = 0 + 0 + 0 + 1 = 1$

- (b) Is df an exact or an inexact differential? Ans. df is an exact differential.

- (c) Calculate the change in the quantity g defined by $dg = ydx$ for the two processes by integrating dg over the paths.

Ans. First process : $x = y \Rightarrow \Delta g = \int_{(0,0)}^{(1,1)} ydx = \int_0^1 ydy = \frac{y^2}{2} \Big|_0^1 = \frac{1}{2}$

Second process : $\Delta g = \int_{(0,0)}^{(1,0)} ydx + \int_{(1,0)}^{(1,1)} ydx = 0 + 0 = 0$

- (d) Is dg an exact or an inexact differential? Ans. dg is an inexact differential.

- (e) Which of the two : f and g , should be called a state function and which one a path function? Why?

Ans. Change in value of f in a process is independent of path, whereas change in value of g depends on path. Hence, f should be called a state function and g a path function.

2. Assuming $U = C_V T$ for a perfect gas, find (i) the internal energy per unit mass and (ii) the internal energy per unit volume, in terms of mass density, pressure and the heat capacity ratio γ .

Ans. Let m be the mass of one molecule, then density, $\rho = \frac{N_A m}{V}$ and $pV = N_A k_B T \Rightarrow \frac{p}{\rho} = \frac{k_B T}{m}$

$\gamma = \frac{C_p}{C_V} \Rightarrow \gamma - 1 = \frac{C_p - C_V}{C_V} = \frac{R}{C_V}$ per mole.

or, per mole $C_V = \frac{R}{\gamma - 1}$; $\therefore U = C_V T = \frac{RT}{\gamma - 1} = \frac{N_A k_B T}{\gamma - 1}$

\therefore internal energy per unit mass $\tilde{u} = \frac{U}{m N_A} = \frac{k_B T}{m} \cdot \frac{1}{\gamma - 1} = \frac{p}{\rho} \cdot \frac{1}{\gamma - 1}$

internal energy per unit volume = $\tilde{u} \cdot \rho = \frac{p}{\gamma - 1}$

3. For a van der Waals gas, obtain an expression for the coefficient of thermal expansion, α . The isothermal compressibility of a substance is defined as $\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$. Why is the negative sign there? Show that $\kappa_T R = \alpha(V_m - b)$, where V_m is the molar volume.

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

We want the value of κ_T to be positive. But, volume decreases on increasing pressure, i.e., if $dp > 0$, then $dV < 0$. Hence, it is convenient to define the quantity with a negative sign in front of the derivative.

For a van der Waals gas, $p = \frac{nRT}{V-nb} - \frac{n^2a}{V^2}$. Differentiating both sides by V and keeping p const., $\frac{nRT}{V-nb} \left(\frac{\partial T}{\partial V} \right)_p - \frac{2n^2a}{V^3} = 0$

$$\therefore \alpha = \frac{1}{V} \cdot \frac{T}{\frac{T}{V-nb} - \frac{2na}{RV^3}(V-nb)} = \frac{RV^2(V-nb)}{RTV^3 - 2na(V-nb)^2}$$

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T = -\frac{1}{V \left(\frac{\partial p}{\partial V} \right)_T} = -\frac{1}{V} \cdot \frac{1}{-\frac{nRT}{(V-nb)^2} + \frac{2n^2a}{V^3}} = \frac{V^2(V-nb)^2}{nRTV^3 - 2n^2a(V-nb)^2}$$

$$\therefore \frac{\kappa_T}{\alpha} = \frac{V-nb}{nR} \implies \kappa_T R = \alpha(V-nb)$$

$$\text{alternatively, } \frac{\kappa_T}{\alpha} = \frac{-\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T}{\frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p} = -\frac{1}{\left(\frac{\partial p}{\partial V} \right)_T \cdot \left(\frac{\partial V}{\partial T} \right)_p} = \left(\frac{\partial T}{\partial p} \right)_V$$

$$p = \frac{nRT}{V-nb} - \frac{n^2a}{V^2} \implies T = \frac{(V-nb)p}{nR} + f(V) \implies \left(\frac{\partial T}{\partial p} \right)_V = \frac{(V-nb)p}{nR}$$

$$\therefore \kappa_T R = \alpha(V-nb).$$

4. A sample of liquid water supercooled to -10°C placed in a thermally insulated compartment undergoes a spontaneous crystallisation to form a mixture of ice and liquid water. Calculate q , w , ΔT , ΔU , ΔH , ΔS for the process.

Ans. thermally insulated compartment, $\therefore q = 0$

\therefore spontaneous crystallisation and the final state has liquid water along with ice,

\therefore final temperature $= 0^\circ\text{C}$ and $\Delta T = 10^\circ$

Let us say there are n moles of water in the sample.

volume of water $= \frac{n \times 18}{\rho}$, where ρ = density of liq. water.

let us consider the path : water (l, -10°C) \longrightarrow water (l, 0°C) \longrightarrow mixture of water(l)+ice, 0°C

There is some decrease in volume in the first step due to anomalous expansion and in the second step there is an increase in volume (11 volumes of water become 12 volumes of ice)

$\therefore \Delta V \approx 0$ (water freezes to a greater volume of ice) and the only work is mechanical, $\therefore w \approx 0$

For the first step, $\Delta U = nC_{V,m,\text{water}} \times 10$ and for the second step, part of the sample freezes releasing enough heat, ($\Delta U = \Delta H - p\Delta V$, p const) so that the ΔU in the first step is canceled (\therefore only part of liq. water freezes).

$\therefore \Delta U$ for the entire process $= 0$

for the first step: $\Delta H \approx \Delta U > 0$ (p const) and say n_1 moles freeze, then for the second step, $\Delta H = -n_1 \Delta_{\text{fus},m} H$

ΔH for the entire process ≈ 0 if the insulation is well maintained

ΔS_{sys} for the first step (calculated for a reversible path)

$$= n \int_{263}^{273} C_{p,m,\text{water}} \frac{dT}{T} \approx 0.075.n. \ln \frac{273}{263} = 0.075 \times 0.037.n = 0.0028.n \text{ kJ/K} > 0.$$

$$\text{For the second step, } \Delta S_{\text{sys}} = \frac{n_1 \Delta_{\text{fus},m} H}{272} = -\frac{n_1 \Delta_{\text{fus},m} H}{272} = -\frac{6.02}{272} n_1 = -0.022.n_1 \text{ kJ/K}$$

overall ΔS_{sys} is a sum of the two terms and we expect it to be negative.

$\Delta S_{\text{universe}} > 0$ \therefore it is spontaneous crystallisation.

the change in chemical potential (Gibbs' free energy) drives the process, $\therefore \Delta G = \Delta H - T\Delta S$

As long as $\Delta G < 0$, the freezing continues and it stops when it reaches the value 0.