EP 2827: Thermodynamics

Homework Set 2*

February 19, 2019

1. The equation of state of a van der Waals gas is,

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nR\theta$$

Compute the volume expansivity, $\beta = \frac{1}{V}\left(\frac{\partial V}{\partial \theta}\right)_P$ and the isothermal compressibility, $\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_\theta$.

(5+5=10 points)

Solution: The van der Waals equation of state is

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nR\theta.$$

Taking partial derivative wrt temperature, θ of both sides at constant pressure, we get,

$$\beta \left[-2\frac{n^2 a\,(V - nb)}{V^2} + \left(\underbrace{P + \frac{n^2 a}{V^2}}_{=\frac{nR\theta}{V-nb}} \right) V \right] = nR,$$

which we can reorganize to obtain,

$$\beta = \frac{RV^2\,(V - n\,b)}{R\theta V^3 - 2na\,(V - nb)^2}.$$

One can check that if we set $a, b = 0$, then it reduces to the ideal gas volume expansivity

$$\beta_{ideal} = \frac{1}{\theta}.$$

Next we rewrite the vdW equation of state as,

$$P = \frac{nR\theta}{V - nb} - \frac{n^2 a}{V^2},$$

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[*] **Due in class on Tuesday Feb. 19th**

and then take partial derivative wrt Pressure, P of both sides at constant temperature, θ to get,

$$1 = -\underbrace{\left(\frac{\partial V}{\partial P}\right)_{\theta}}_{=\kappa V}\left(\frac{nR\theta}{(V-nb)^2} - 2\frac{n^2 a}{V^3}\right),$$

which we reorganize to obtain,

$$\kappa = \frac{V^2 (V-nb)^2}{nR\theta V^3 - 2na(V-nb)^2}.$$

Again, a check that the expression is correct that setting $a = 0, b = 0$ reproduces the ideal gas compressibility,

$$\kappa_{ideal} = \frac{V}{nR\theta} = \frac{1}{P}.$$

2. For a hydrostatic system undergoing a quasistatic process, show that the change in pressure,

$$dP = \frac{\beta}{\kappa}d\theta - \frac{1}{\kappa V}dV.$$

This is useful for the cases when measuring (changes) in volume and temperature is straightforward but measuring pressure isn't, e.g. block of solid. A block of Copper at pressure of 1 atm, a volume of $100 cm^3$ and at a temperature of 10° C is experiences a rise in temperature of 5° C and an increase in volume of $0.005 cm^3$. Assuming the volume expansivity remains 4.95×10^{-5} K^{-1} and isothermal compressibility to be 6.17×10^{-12} Pa^{-1} in the range of temperature 0 – 20° C.

(5+5=10 points)

Solution: Taking P to be a function of V and θ, we get,

$$dP = \left(\frac{\partial P}{\partial \theta}\right)_V d\theta + \left(\frac{\partial P}{\partial V}\right)_{\theta} dV.$$

Next we rewrite the coefficients, $\left(\frac{\partial P}{\partial V}\right)_{\theta}$ and $\left(\frac{\partial P}{\partial \theta}\right)_V$ as follows,

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

and,

$$\left(\frac{\partial P}{\partial \theta}\right)_V = -\frac{1}{\left(\frac{\partial \theta}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_{\theta}} = \frac{\frac{1}{V}\left(\frac{\partial V}{\partial \theta}\right)_P}{-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{\theta}} = \frac{\beta}{\kappa}.$$

Substituting this in the rhs of the expression for dP, we obtain,

$$P = \frac{\beta}{\kappa}d\theta - \frac{1}{\kappa V}dV.$$

(This part carries 5 points, 2 points for the correct $\left(\frac{\partial P}{\partial V}\right)_{\theta}$ and 2 points for the correct $\left(\frac{\partial P}{\partial \theta}\right)_V$ expression and 1 for the final result).

For processes where β and κ remain unchanged the expression dP can be easily integrated to compute finite amount change,

$$\Delta P = \frac{\beta}{\kappa}\Delta\theta - \frac{1}{\kappa V}dV$$

Plugging in the data: $\Delta\theta = 5K$, $\Delta V = 0.005cm^3, \beta = 4.95 \times 10^{-5}K^{-1}, \kappa = 6.17 \times 10^{-12}Pa^{-1}, V = 100cm^3$, we get,

$$\begin{aligned} \Delta P &= \frac{4.95 \times 10^{-5}K^{-1}}{6.17 \times 10^{-12}Pa^{-1}}(5\,K) - \frac{1}{(6.17 \times 10^{-12}Pa^{-1}) \times 100cm^3}(0.005)\,cm^3 \\ &= 4.01 \times 10^7 Pa - 8.10 \times 10^{-6} Pa \\ &\approx 4.01 \times 10^7 Pa. \end{aligned}$$

(This numerical carries 5 points, for algebraic errors at least 1 point should be deducted).

3. Calculate the work done on one mole of van der Waals gas quasistatically and isothermally from volume, V_i to volume, V_f.

(5 points)

Solution: First we express the pressure, P of a vdW gas in terms of V and θ,

$$P = \frac{nR\theta}{V - nb} - \frac{n^2 a}{V^2}.$$

The isothermal work done on the vdW gas is given by,

$$\begin{aligned} W_{isothermal} &= -\int_{V_i}^{V_f} PdV \\ &= -\int_{V_i}^{V_f} dV \left(\frac{nR\theta}{V - nb} - \frac{n^2 a}{V^2}\right) \\ &= -nR\theta \ln\left(\frac{V_f - nb}{V_i - nb}\right) + n^2 a\left(\frac{1}{V_i} - \frac{1}{V_f}\right). \end{aligned}$$

Note that according to the convention we are following, work done *on* the system is positive (consequently work done *by* the system is negative). So be careful about the sign. Also note that when a, b are set to zero, this reduces to the expression for isothermal work done on an ideal gas.

4. The pressure on 100 g block of Nickel is increased quasistatically and isothermally from 0 to 500 atm. Assuming the density and compressibility to remain constant at values 8.90×10^3 kg/m^3 and 6.75×10^{-12} Pa^{-1} respectively, calculate the work done.

(5 points)

Solution: We start from,

$$dP = \frac{\beta}{\kappa}d\theta - \frac{1}{\kappa V}dV$$

For isothermal process this becomes,

$$dP = -\frac{1}{\kappa V} dV \implies dV = -\kappa V dP.$$

So the work done is,

$$W = -\int P dV = \kappa V \int P\, dP = \frac{\kappa V}{2}\left(P_f^2 - P_i^2\right)$$

Substituting the volume to be, $V = mass/density = m/\rho$, we get the work done,

$$W = \frac{\kappa m}{2\rho}\left(P_f^2 - P_i^2\right).$$

Plugging $\kappa = 6.75 \times 10^{-12}\, Pa^{-1}$, $m = 100g = 0.1\, kg$, $\rho = 8.90 \times 10^3\, kg/m^3$ and $P_f = 500\, atm = 5.07 \times 10^7 Pa$ and $P_i = 0$,

$$W = \frac{6.75 \times 10^{-12} \times 0.1}{2 \times 8.90 \times 10^3}\left(5.07 \times 10^7\right)^2 = 9.75 \times 10^{-2} J.$$

5.

Show that work done during a quasistatic isothermal change of state of a paramagnetic substance obeying Curie's law is,

$$W = \frac{\mu_0 \theta}{2C_c}\left(M_f^2 - M_i^2\right) = \frac{\mu_0 C_C}{2\theta}\left(\mathcal{H}_f^2 - \mathcal{H}_i^2\right).$$

(5 points)

Solution:
Work done on a paramagnetic substance is given by,

$$dW = \mu_0 \mathcal{H}\, dM$$

We use Curie's law to substitute for $\mathcal{H}$,

$$\mathcal{H} = \frac{\theta}{C_C} M,$$

to obtain the expression for infinitesimal work done,

$$dW = \mu_0 \frac{\theta}{C_C} M\, dM.$$

Isothermal work done is then,

$$W_{isothermal} = \int_{M_i}^{M_f}\left(\mu_0 \frac{\theta}{C_C} M\, dM\right) = \frac{\mu_0 \theta}{C_C}\int_{M_i}^{M_f} M\, dM = \frac{\mu_0 \theta}{2C_c}\left(M_f^2 - M_i^2\right).$$

Again we can use Curie's law to replace $M_{i(f)} = C_C \mathcal{H}_{i(f)}/\theta$ to get,

$$W = \frac{\mu_0 \theta}{2C_c}\left(M_f^2 - M_i^2\right) = \frac{\mu_0 C_C}{2\theta}\left(\mathcal{H}_f^2 - \mathcal{H}_i^2\right).$$