THERMAL AND KINETIC PHYSICS 2010, (PHY 214)

Outline Solutions to Coursework 9 :   Week 10

QUESTION 1: (24 marks)

(a) For work done ON the elastic, $dW = \mathcal{F}dL$ The First Law and the Thermodynamic Identity can then be written;

$$dU = dQ + dW = TdS + \mathcal{F}dL$$

From the definition of the Helmholtz free energy, $F = U - TS$, we have for the infinitesimal change in F;

$$dF = dU - TdS - SdT = TdS + \mathcal{F}dL - TdS - SdT = -SdT + \mathcal{F}dL$$

$$dF = -SdT + \mathcal{F}dL \qquad\qquad \textbf{[2mks]}$$

which implies that the natural variables for F are T and L, $F = F(T, L)$.

As a function of T and L we can write for the differential of F

$$dF = \left(\frac{\partial F}{\partial T}\right)_L dT + \left(\frac{\partial F}{\partial L}\right)_T dL \qquad\qquad \textbf{[1mk]}$$

and comparing the two expressions for dF we obtain the relations

$$-S = \left(\frac{\partial F}{\partial T}\right)_L \qquad\qquad \mathcal{F} = \left(\frac{\partial F}{\partial L}\right)_T \qquad\qquad \textbf{[1mk]}$$

Since F is a function of a state dF is a perfect differential and therefore the mixed second derivative is independent of the order in which we calculate It. We may therefore deduce

$$\frac{\partial^2 F}{\partial L \partial T} = \frac{\partial^2 F}{\partial T \partial L}$$

Or, using our relations between physical variables and partial differentials of F wrt its natural variables found earlier

$$\frac{\partial^2 F}{\partial L \partial T} = \frac{\partial}{\partial L}\left(\frac{\partial F}{\partial T}\right)_L = -\left(\frac{\partial S}{\partial L}\right)_T = \frac{\partial^2 F}{\partial T \partial L} = \frac{\partial}{\partial T}\left(\frac{\partial F}{\partial L}\right)_T = \left(\frac{\partial \mathcal{F}}{\partial T}\right)_L$$

which is the Maxwell relation

$$-\left(\frac{\partial S}{\partial L}\right)_T = \left(\frac{\partial \mathcal{F}}{\partial T}\right)_L \qquad \textbf{[1mk]}$$

From the equation of state we can calculate

$$\left(\frac{\partial \mathcal{F}}{\partial T}\right)_L = a\left[\frac{L}{L_0} - \left(\frac{L_0}{L}\right)^2\right]$$

which is greater than zero (positive) if $L > L_0$. Thus, from the Maxwell relation

$$\left(\frac{\partial S}{\partial L}\right)_T = -\left(\frac{\partial \mathcal{F}}{\partial T}\right)_L < 0 \qquad \textbf{[2mks]}$$

The elastic band is made of long carbon chains or macromolecules which in equilibrium will curl up into balls to maximise their entropy. When we stretch the jumbled up macromolecules, we pull them out into an arrangement that more closely resembles a straight line and when they are elongated there are fewer arrangements possible for the subunits so they are more ordered and have lower entropy than when unstretched. Imagine a string of pearls either curled up or straightened out. The latter arrangement has fewer possible ways of being achieved and thus a lower entropy.

$$\textbf{[2mks]}$$

(b)   Consider a small change in length dL at constant T. Dividing the First Law expression by dL and remembering that T is constant gives

$$\left.\frac{dU}{dL}\right|_T = T\left.\frac{dS}{dL}\right|_T + \mathcal{F} \qquad \textbf{[1mk]}$$

but these ratios just define partial derivatives so we have

$$\left(\frac{\partial U}{\partial L}\right)_T = T\left(\frac{\partial S}{\partial L}\right)_T + \mathcal{F} = -T\left(\frac{\partial F}{\partial T}\right)_L + \mathcal{F} \qquad \text{[3mks]}$$

where we have used the Maxwell relation.

(c) Using $\left(\frac{\partial F}{\partial T}\right)_L$ as calculated in (a) above and using the equation of state to give $\mathcal{F}$

gives

$$\left(\frac{\partial U}{\partial L}\right)_T = -Ta\left[\frac{L}{L_0} - \left(\frac{L_0}{L}\right)^2\right] + aT\left[\frac{L}{L_0} - \left(\frac{L_0}{L}\right)^2\right] = 0 \qquad \text{[3mks]}$$

Hence U has no dependence on L and is a function of T only, $U = U(T)$. **[2mks]**

(d) The heat capacity C_L is defined as $C_L = T\left(\frac{\partial S}{\partial T}\right)_L$

If we knew the partial derivative $\left(\frac{\partial T}{\partial L}\right)_S$ we could estimate the change of temperature

by $\Delta T \approx \left(\frac{\partial T}{\partial L}\right)_S \Delta L$, so we must find this derivative.

By the cyclical identity we have

$$\left(\frac{\partial T}{\partial L}\right)_S \left(\frac{\partial L}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_L = -1 \qquad \text{[1mk]}$$

We re-express this as

$$\left(\frac{\partial T}{\partial L}\right)_S = \frac{-1}{\left(\frac{\partial L}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_L} = -\frac{\left(\frac{\partial S}{\partial L}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_L} = \frac{T}{C_L}\left(\frac{\partial \mathcal{F}}{\partial T}\right)_L \qquad \text{[2mks]}$$

where we have used the reciprocal identity, the Maxwell identity and the definition of C_L. Thus we have

$$\left(\frac{\partial T}{\partial L}\right)_S = \frac{aT}{C_L}\left[\frac{L}{L_0} - \left(\frac{L_0}{L}\right)^2\right]$$
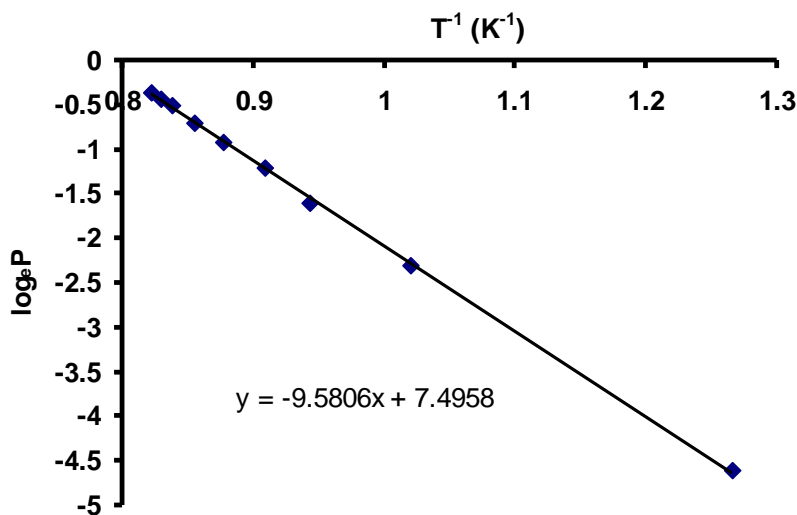
[1mk]

which we evaluate for $L_0 = 1$m, $L = 1.5$m giving

$$\left(\frac{\partial T}{\partial L}\right)_S = \frac{1.3\times10^{-2}NK^{-1}300K}{1.2JK^{-1}}\left[\frac{1.5m}{1m} - \left(\frac{1m}{1.5m}\right)^2\right] = 3.43Km^{-1}$$

$$\Delta T \approx \left(\frac{\partial T}{\partial L}\right)_S \Delta L = 3.43Km^{-1} \times 0.1m = 0.34K$$

[2mks]

QUESTION 2: (16 marks)

(a) Using the data given we may begin by plotting lnP against 1/T .
This shows an excellent linear relationship.

[8mks]

(b) From the relation $\ln P = -\dfrac{\ell^{L\rightarrow V}}{R} + const$ we note that the slope of the graph lnP

vs $\dfrac{1}{T}$ is $slope = \dfrac{\ell^{L\rightarrow V}}{R}$

[2mks]

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we estimate the slope either by using a computer fitting routine, or by taking the initial and final data points and calculating

$$slope = \frac{\ln P_f - \ln P_i}{\frac{1}{T_f} - \frac{1}{T_i}} = \frac{-4.605 + 0.357}{1.266 - 0.822} = \frac{-4.248}{0.444} = -9.57 \qquad \textbf{[3mks]}$$

And therefore we find

$$\frac{\ell^{L \to V}}{R} = -slope = 9.57$$

$$\ell^{L \to V} = 9.57 \times 8.31 Jmol^{-1}K^{-1} = 79.52 Jmol^{-1} \qquad \textbf{[3mks]}$$

NB going from liquid to vapour involves an increase in disorder an increase in entropy and therefore $\ell^{L \to V}$ must be positive as found.