EXAM 2

16 October 2003

IMPORTANT: Write clearly and neatly. Make sure that you give some reasoning or working for each answer. Full marks will NOT be awarded for the final answer by itself, UNLESS it is supported by a brief justification or explanation.

Give units for all numerical quantities!

Some data: $R = 8.314$ J K^{-1} mol^{-1} 1 atm = 101325 Pa $N_A = 6.022 \times 10^{23}$ mol^{-1}

$k = 1.38 \times 10^{-23}$ J K^{-1} mol^{-1} 1 amu = 1.66×10^{-27} kg

Your name SOLUTIONS

(1) *33 points*

i) Write down the definitions of the expansion coefficient α and the isothermal compressibility κ_T.

ii) By considering V as a general function of p and T, write out an expression for dV in terms of dp and dT.

iii) Assume V is constant and thus obtain the relationship between α, κ_T and $(\partial p/\partial T)_V$.

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

$$dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp$$

V const so $dV = 0$. Divide by dT:

$$0 = \left(\frac{\partial V}{\partial T}\right)_p + \left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V$$

$$= V.\alpha - V\kappa_T \left(\frac{\partial p}{\partial T}\right)_V$$

$$\therefore \left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa_T}$$

See exercise 3.12

(2) *33 points*

A certain process causes a change in entropy of the system of -33 J K^{-1}. During this process the system lost 15 kJ of heat to the surroundings, which maintained a temperature of 400 K.

i) Explain carefully if the process is reversible, and why.

ii) Comment on the possibility of the system instead losing 10 kJ of heat for the same change of state in the system.

i) $\Delta S_{surr} = \frac{15000 \text{ J}}{400 \text{ K}} = 37.5 \text{ JK}^{-1}$

$\Delta S_{uni} = \Delta S_{surr} + \Delta S_{sys} = (-33 + 37.5) \text{ JK}^{-1}$

> 0

$\therefore$ a spontaneous change.

ii) ΔS_{surr} would be $\frac{10000 \text{ J}}{400 \text{ K}} = 25 \text{ JK}^{-1}$

which would imply $\Delta S_{uni} < 0$.

This is impossible.

see Exercise 4.10

(3) *34 points*

Determine the absolute entropy of kryptonite at 0 and 600 K, given the following information:

melting point 500 K

$C_p(0\text{-}500\ K) = 10T + 0.01T^2\ J\ K^{-1}\ mol^{-1}$

$C_p(500\text{-}1000\ K) = 25 + 0.003T^2\ J\ K^{-1}\ mol^{-1}$

$\Delta_{fus}H = 21\ kJ\ mol^{-1}$.

At 0K the entropy is zero by the 3rd Law.

$$S_{600} = \int_0^{600} \frac{C_p\,dT}{T} + \int \frac{q_{\text{phase change}}}{T_{\text{phase change}}}$$

$$= \int_0^{500} (10 + 0.01\,T)\,dT + \int_{500}^{600} \left(\frac{25}{T} + 0.003T\right)dT + \frac{21000\ J}{500\ K}$$

$$= \left[10T + 0.005T^2\right]_0^{500} + \left[25\ln T + 0.0015T^2\right]_{500}^{600} + \frac{21000}{500}$$

$$= 5000 + 1250 - 0 - 0 + 159.9 + 540 - 155.4 - 375 + 42$$

$$= 6461.5\ J\ K^{-1}\ mol^{-1}.$$