EXAM 2

13 October 2002

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) *34 points*

i) By considering V as a function of p and T, write out an expression for dV in terms of dp and dT. Use this expression to derive an expression for d (ln V) in terms of the expansion coefficient and isothermal compressibility.

ii) The Joule-Thompson coefficient for a gas is $\mu = (\partial T/\partial p)_H$. By considering H as a function of p and T, prove that $(\partial H/\partial p)_T = -C_p \mu$.

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

$$d \ln V = \frac{1}{V} dV = \frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T dp + \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p dT$$

$$= -\kappa_T \quad + \alpha$$

ii) $H = H(p,T)$ so $dH = \left(\frac{\partial H}{\partial p}\right)_T dp + \left(\frac{\partial H}{\partial T}\right)_p dT$

divide by dp, hold H constant (so dH=0)

$$0 = \left(\frac{\partial H}{\partial p}\right)_T + \underbrace{\left(\frac{\partial H}{\partial T}\right)_p}_{C_p} \underbrace{\left(\frac{\partial T}{\partial p}\right)_H}_{\mu}$$

$$\therefore \left(\frac{\partial H}{\partial p}\right)_T = -C_p \cdot \mu$$

(2) *33 points*

1 mol of water vapor at 360 K and 1 atm is spontaneously condensed at constant pressure and temperature. Find ΔS and ΔG for the system.

Data: $\Delta_{vap}H$ varies with T and is 41.00 kJ mol^{-1} at 373 K. $C_p(H_2O\ (g)) = 30.0$ J K^{-1} mol^{1} (independent of T) and $C_p(H_2O\ (l)) = 75.0$ J K^{-1} mol^{-1} (independent of T). The boiling point of water is 373 K.

To define ΔS we need a reversible path:

$$\begin{tikzcd}
H_2O(g),\ 360K \arrow[r, "1"] \arrow[d] & H_2O(g),\ 373K \arrow[d, "2"] \\
H_2O(l),\ 360K & H_2O(l),\ 373K \arrow[l, "3"']
\end{tikzcd}$$

1: $\Delta S = \int_{360}^{373} dq_{rev}/T = \int_{360}^{373} C_p\, dT/T = 30 \ln\left(\frac{373}{360}\right) JK^{-1} = 1.064\ JK^{-1}.$

2. Condensation reversible at 373K: $\Delta S = \Delta H/T = \frac{-41000\,J}{373K} = -109.920\ JK^{-1}.$

3. $\Delta S = \int_{373}^{360} C_p\, dT/T = 75 \ln(360/373) = -2.661\ JK^{-1}.$

Total ΔS = $1.06 - 109.92 - 2.66\ JK^{-1} = \underline{-111.52\ JK^{-1}}.$

We need ΔH. Could evaluate along the same path, or equivalently

$$\Delta H_{vap}(360K) = \Delta_{vap}H(373K) + \int_{373}^{360} \Delta C_p . dT \quad . \quad \Delta C_p = C_{p\,gas} - C_{p\,liquid} \text{ here.}$$

$$= 41\,000 + (30-75)(360-373)\ J$$

$$= 41585\ J$$

ΔH for condensation is -41585 J.

$$\Delta G = \Delta H - T\Delta S = -41585 - (360 \times -111.52)\ J$$

$$= -1438\ J$$

$$= \underline{-1.44\ kJ}.$$

(3) *33 points*

1 mol of an ideal gas (the system) has $C_V = 25\ \mathrm{J\,K^{-1}}$. It is initially at 200 K and has a pressure of 1×10^6 Pa. It is expanded isothermally against a constant external pressure of 1×10^5 Pa until the gas pressure is 1×10^5 Pa.

Calculate q, w, ΔU, ΔH, ΔG, ΔA, ΔS and $\Delta S_{universe}$ (i.e. the total ΔS). Explain if this process is spontaneous.

Initial volume $V_1 = \frac{nRT_1}{P_1} = \frac{1 \times 8.314 \times 200}{10^6}\ m^3 = 1.663 \times 10^{-3}\ m^3$

Final volume $V_2 = \frac{nRT_2}{P_2}$ isothermal so $T_2 = T_1$

$= \frac{8.314 \times 200}{1 \times 10^5}\ m^3 = 1.663 \times 10^{-2}\ m^3$.

$w = -P_{ex}(V_2 - V_1) = -10^5 \times (0.01497)$ J

$= -1497$ J.

Isothermal ∴ $0 = \Delta U = q + w$ ∴ $q = -w = +1497$ J.

$\Delta H = 0$.

If the change was reversible, $\Delta S = R\ln\left(\frac{V_2}{V_1}\right) = R\ln 10$
$= 19.14\ JK^{-1}$.

Applies generally by fn. of state argument.

$\Delta A = \Delta U - T\Delta S = -3829$ J.

$\Delta G = \Delta H - T\Delta S = -3829$ J.

Heat transfer into surroundings $= -q = -1497$ J. Because surroundings so large, treat this as reversible for the surroundings

∴ $\Delta S_{surr} = q_{rev}/T = -1497/200\ JK^{-1} = -7.49\ JK^{-1}$.

$\Delta S_{uni} = \Delta S + \Delta S_{surr} = +11.65\ JK^{-1}$

> 0 ∴ spontaneous.