EXAM 1

20 September 1996

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 quantities!

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

kinetic energy is half mass x speed^2 $k_B = R/N_A$

Molar masses of He, H_2 & O_2 are 0.004, 0.002 & 0.032 kg mol^{-1}.

Volume of a sphere is $4/3\ \pi\ r^3$

(1) *20 points*

A ballon of radius 3 m is filled with He and at sea-level the temperature is 298 K and the pressure is 10^5 Pa. It is released and floats to an altitude where the radius is now 5 m and the temperature is 250 K. What is the new pressure in the balloon?

(2) *30 points*

a) Define the *compression factor*, Z, for a gas.

b) The equation of state for 1 mole of an imaginary gas is

$$p = \frac{RT}{V-b} - \frac{a}{V}$$

Calculate Z for this gas when $V = 0.002$ m^3 and $T = 500$ K, given $a = 500$ m^3 Pa and $b = 5 \times 10^{-4}$ m^3. Based on your answer, explain if attractive or repulsive forces are dominating under these conditions.

c) Work out an expression for dp/dV.

(3) *30 points*

The average kinetic energy ε of ideal gas molecules is given by $\varepsilon = 3k_BT/2$. Consider samples of H_2 and O_2 at the same T.

a) What are the average kinetic energies of (i) H_2 and (ii) O_2 molecules at 400 K?

b) What are the root mean square molecular speeds of (i) H_2 and (ii) O_2 molecules at 400 K?

c) How would your answers to (b) change if the temperature was increased to 3600 K?

(4) *20 points*

a) A gas mixture at 200 K contains 0.001 kg of H_2 and 0.001 kg of O_2. The total pressure is 1×10^4 Pa. Calculate the the partial pressures of H_2 and O_2, and the volume of the container.

b) Starting from the ideal gas law, derive an expression for the density of an ideal gas in terms of the molar mass, T, p and other constants.

EXAM 2

18 October 1996

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 quantities! ***YOUR NAME*** ______________________________

Some data: $R = 8.314$ J K^{-1} mol^{-1} 1 atm = 101325 Pa $N_A = 6.022 \times 10^{23}$ mol^{-1} $\gamma = C_p/C_V$
$C_p - C_V = nR$ $dU = dq + dw$ $dS = dq/T$ $H = U + pV$ $G = H - TS$ $A = U - TS$

(1) *25 points*

1 mole of an ideal gas is expanded reversibly and isothermally at temperature T from V_1 to V_2. Find q, w, ΔU, ΔH, ΔS and ΔG for this system clearly stating any results you rely on, and showing your work.

(2) *25 points*

Consider the hydrogenation of benzene to form cyclohexane:

$$C_6H_6(l) + 3\,H_2(g) \rightarrow C_6H_{12}(l)$$

ΔH for combustion to $CO_2(g)$ and/or $H_2O(l)$ at 298 K for C_6H_6, C_6H_{12} and H_2 is -3270, -4000 and -286 kJ mol^{-1}, respectively. C_p for C_6H_6, H_2 and C_6H_{12} is 100 + 0.3 T, 20 + 0.05 T and 110 + 0.2 T J K^{-1} mol^{-1}, respectively.

i) Show that ΔH for hydrogenation at 298 K is 128 kJ mol^{-1}.

ii) Deduce ΔU for hydrogenation at 298 K.

iii) Deduce ΔH for hydrogenation at 50 K.

(3) *25 points*

Imagine that at 1 atm pressure 1 mol of liquid water (the system) reversibly freezes at 273 K, and 6000 J of heat are released. What are ΔS_{sys}, ΔS_{surr}, ΔS_{uni} and ΔG_{sys}? How would the latter two quantities change (if at all), *qualitatively*, if you analyzed the freezing of water at a lower temperature?

(4) *25 points*

1 mol of ideal gas expands reversibly and adiabatically from 1 m^3 to 3 m^3 and its temperature drops from 400 to 300 K. $C_p = 21$ J K^{-1} mol^{-1}. Calculate ΔU, q, w and ΔS.

EXAM 3

15 November 1996

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 quantities! *YOUR NAME* _________________________

Some data: $R = 8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}$ $1\ \mathrm{atm} = 101325\ \mathrm{Pa}$ $N_A = 6.022 \times 10^{23}\ \mathrm{mol^{-1}}$ $\gamma = C_p/C_V$
$C_p - C_V = nR$ $dU = dq + dw$ $dS = dq/T$ $H = U + pV$ $G = H - TS$ $A = U - TS$

(1) *30 points*

i) Starting with an expression for dG in terms of p, V, T and S, derive the result $(\partial V/\partial T)_p = -(\partial S/\partial p)_T$.

ii) Hence determine ΔS for the isothermal expansion of 1 mole of a non-ideal gas accomplished by reducing the pressure from p_1 to p_2. The equation of state for 1 mole of this gas is $p = (RT/V) - a$.

(2) *30 points*

At 1000 K, $\Delta G°$ for the reaction $SO_2(g) + H_2O(g) = SO_3(g) + H_2(g)$ is $-5\ \mathrm{kJ\ mol^{-1}}$.

i) What is the equilibrium constant K?

ii) Assuming ideal gas behavior, suppose 2 mol of SO_2 and 2 mol of H_2O are heated in a container to 1000 K. What are the equilibrium amounts of SO_2, H_2O, SO_3 and H_2?

iii) If you started with 1 mol SO_2, 3 mol H_2O, 2.5 mol SO_3 and 2.5 mol H_2, what is the spontaneous direction of reaction? **You must show work.**

(3) *30 points*

i) Starting from the Clausius-Clapeyron equation for the evaporation of a liquid,

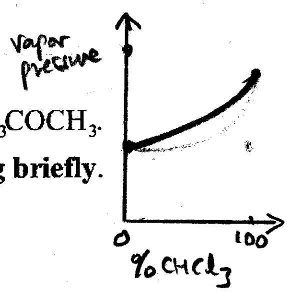
$$\frac{d\ln p}{dT} = \frac{\Delta_{vap}H}{RT^2}$$

and the assumption that $\Delta_{vap}H$ is independent of temperature, find $\ln(p_2/p_1)$ as function of $\Delta_{vap}H$, T_1 and T_2, where p_1 and p_2 are the vapor pressures at temperatures T_1 and T_2.

ii) Water boils at 100 °C at 10^5 Pa pressure. Use your result to part (i) to find $\Delta_{vap}H$ given that the boiling point is 75 °C at the top of Mount Everest, where the atmospheric pressure is 4×10^4 Pa.

(4) *10 points*

Here is a plot of vapor pressure as function of composition for mixtures of $CHCl_3$ and CH_3COCH_3.



i) Is the deviation from Raoult's Law positive or negative? **Explain your reasoning briefly.**

ii) Interpret this deviation in terms of intermolecular forces in the system.