EXAM 1

28 September 1999

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

(1)   *33 points*

a) 1 mol of gas follows the equation of state

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

Use this information to derive the second and third virial coefficients for the gas. HINTS: The virial equation is $p = RT/V \{1 + B/V + C/V^2 + ...\}$ and $1/(1-x) = 1 + x + x^2 + ...$

b) Given that $b = 4 \times 10^{-5} \text{ m}^3$ for 1 mol, estimate the molecular diameter of the gas molecules.

c) Deduce the compression factor for the gas when $V = 2 \times 10^{-4} \text{ m}^3$ and $T = 300$ K. In a few lines, explain in terms of a molecular interpretation why your answer is greater than or smaller than the value expected for an ideal gas.

a) $p = \dfrac{RT}{V\left(1-\frac{b}{V}\right)} = \dfrac{RT}{V}\left(1 + \frac{b}{V} + \frac{b^2}{V^2} + ...\right)$ so $B = b$ and $C = b^2$.

b) $b \approx \frac{16}{3}\pi r^3 \cdot N_A$ $\therefore$ $r^3 = \dfrac{3 \cdot 4 \times 10^{-5} \text{ m}^3}{16\pi \times 6.022 \times 10^{23}} = 4.0 \times 10^{-30} \text{ m}^3$

$\therefore r = 1.6 \times 10^{-10} \text{ m}$ and   diameter $= 2r = 3.2 \times 10^{-10} \text{ m}$.

c) $z = \dfrac{pV}{RT} = \dfrac{RT}{V-b} \cdot \dfrac{V}{RT} = \dfrac{V}{V-b} = \dfrac{2 \times 10^{-4}}{2 \times 10^{-4} - 4 \times 10^{-5}} = 1.25$

$z > 1$ showing that intermolecular repulsions dominate.

(2)   *34 points*

C_p for 1 mol of an ideal gas obeys the equation $C_p = (13 + 500/T)$ J K^{-1} where T is absolute temperature in kelvin. Calculate q, w, ΔU and ΔH when the temperature is reversibly raised from 298 to 500 K

a) At constant volume.

(see Exercise 2.11)

b) At constant pressure.

c) Adiabatically.

a) Const. vol. so $w=0$, $\Delta U = q + w = q$ here.

$$dU = C_v dT \quad \therefore \quad \Delta U = \int_{T_1}^{T_2} C_v dT = \left[4.686\,T + 500\,\ln T \right]_{298}^{500} = 1206 \text{ J} = q.$$

$$dH = C_p dT \quad \therefore \quad \Delta H = \int_{T_1}^{T_2} C_p dT = \left[13\,T + 500\,\ln T \right]_{298}^{500} = 2885 \text{ J}.$$

b) ΔU, ΔH same as before (ideal gas).

At const. press. $q = \Delta H = 2885$ J.

$\Delta U = q + w \quad \therefore \quad w = \Delta U - q = -1679$ J.

c) ΔU, ΔH same as before.

$q = 0$ and $\Delta U = q + w \quad \therefore \quad w = \Delta U$ here $= +1206$ J.

(3) 33 points

Use the following information all at 298 K to predict the enthalpy of formation of $Si_2H_6(g)$ at 400 K.

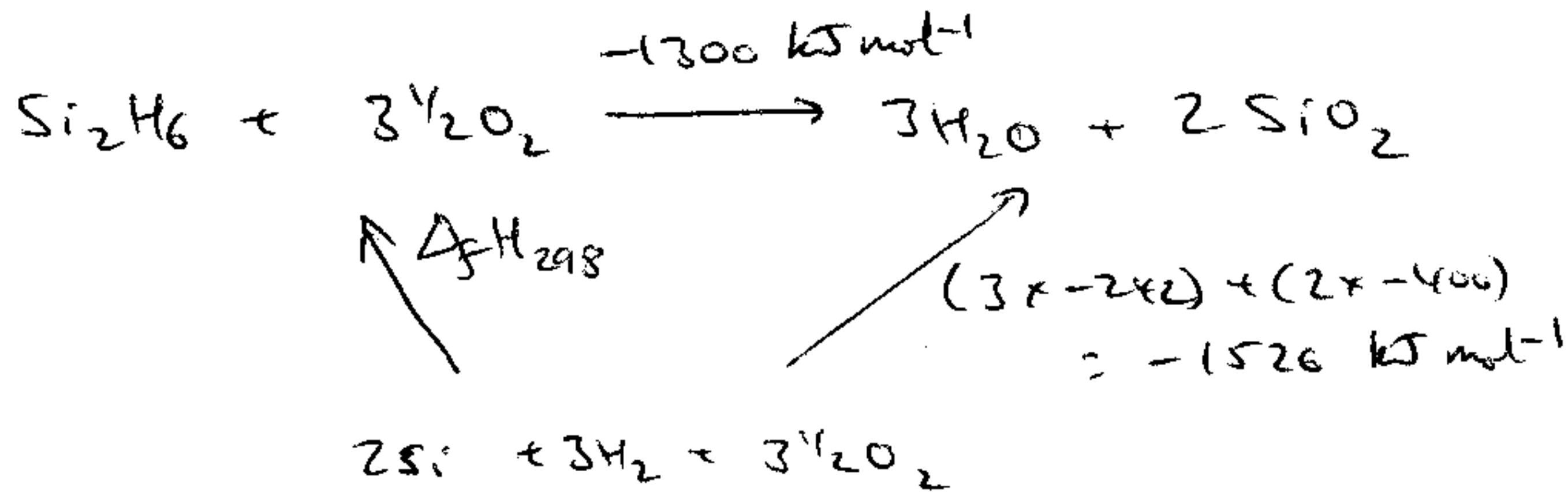$C_p(Si(s)) = 20$ J K^{-1} mol^{-1}. $C_p(H_2(g)) = 25$ J K^{-1} mol^{-1}. $C_p(Si_2H_6(g)) = 35$ J K^{-1} mol^{-1}.

ΔH for $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$ -242 kJ mol^{-1}.

ΔH for $Si(s) + O_2(g) \rightarrow SiO_2(s)$ -400 kJ mol^{-1}.

ΔH for $Si_2H_6(g) + 3\frac{1}{2} O_2(g) \rightarrow 3H_2O(l) + 2SiO_2(s)$ -1300 kJ mol^{-1}.

(see exercise 2.29)

$$Si_2H_6 + 3\tfrac{1}{2}O_2 \xrightarrow{-1300 \text{ kJ mol}^{-1}} 3H_2O + 2SiO_2$$

$\uparrow \Delta_f H_{298}$ $\nearrow$ $(3 \times -242) + (2 \times -400)$
                                                   $= -1526$ kJ mol^{-1}

$$2Si + 3H_2 + 3\tfrac{1}{2}O_2$$

$\Delta_f H_{298} - 1300 = -1526$ $\therefore$ $\Delta_f H_{298} = -226$ kJ mol^{-1}.

Note this is ΔH_{298} for $2Si + 3H_2 \rightarrow Si_2H_6$ <u>at 298 K</u>.

ΔC_p for this reaction is $35 - 3\times25 - 2\times20 = -80$ J K^{-1} mol^{-1}.

$$\Delta H_{400} = \Delta H_{298} + \int_{298}^{400} \Delta C_p \, dT = \Delta H_{298} + \int_{298}^{400} -80 \, dT$$

$$= -226 - \frac{80}{1000}(400 - 298) \text{ kJ mol}^{-1}$$

$$= -226 - 8.2 \text{ kJ mol}^{-1}$$

$$= -234 \text{ kJ mol}^{-1}.$$