EXAM 1

26 September 1994

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 $N_A = 6.022$ x 10^{23} mol^{-1}

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

Molar masses of He, H_2 & I_2 are 0.004, 0.002 & 0.128 kg mol^{-1}.

(1)   *25 points*

a)   Define the *compression factor*, Z, for a gas. Sketch a plot of Z versus p for a typical gas, out to roughly a thousand atm, and *qualitatively* explain positive and negative deviations from ideality in terms of intermolecular forces.

b)   The equation of state for 1 mole of a van der Waals gas is

Calculate Z for this gas when $V = 0.001$ m^3 and $T = 298$ K, given $a = 0.5$ m^6 Pa and $b = 5$ x 10^{-5} m^3.

$$p = \frac{RT}{V-b} - \frac{a}{V^2}$$

c)   Give an approximate physical interpretation of the 'b' parameter.

(2)   *25 points*

Ethane, $C_2H_6(g)$, was completely burned to $CO_2(g)$ and $H_2O(l)$ at 300 K in a sealed calorimeter, and 500 kJ mol^{-1} of heat were evolved. Derive ΔU and ΔH for the combustion reaction at this temperature (treat the gases as ideal).

3)   *25 points*

a)   Starting with the ideal gas equation of state and the result that $pV = Nmc^2/3$, where N is the number of molecules, m is their mass and c^2 the mean square speed, <u>derive</u> the result $\varepsilon = 3k_BT/2$ for the average kinetic energy ε of the molecules.

b)   What is the average kinetic energy of He atoms at 400 K?

c)   Consider samples of H_2 and I_2 at 500 K. What are the ratios of (i) the average molecular kinetic energies, and (ii) the root mean square molecular speeds?

(4)   *25 points*

a)   Sketch a p versus V diagram for a real gas (that can liquefy), and mark the four areas that correspond to the phases gas, liquid, liquid plus vapor, and supercritical fluid. Label the critical point.

b)   Starting from the equation of state for a van der Waals gas (Q.1), obtain the first and second derivatives of p with respect to V at fixed T, in terms of V, T and constants.

c)   What are the numerical values of these two derivatives at the critical point?

EXAM 2

24 October 1994

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 information: $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ $1 \text{ atm} = 101325 \text{ Pa}$ $\gamma = C_p/C_v$ $C_p - C_v = nR$

(1)   *35 points.*

i)   Define $\Delta_f H^\circ$ and C_p for a substance.

ii)   The enthalpy of combustion of propane, $C_3H_8(g)$, is $-2000 \text{ kJ mol}^{-1}$, and $\Delta_f H^\circ$ for $CO_2(g)$ and $H_2O(l)$ are -400 and -300 kJ mol^{-1}, respectively. Use these data to show that $\Delta_f H^\circ$ for propane is -400 kJ mol^{-1} at 298 K.

iii) C_p for graphite, propane and H_2 are 9, 74 and $29 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively, and may be assumed to be temperature-independent. Find $\Delta_f H^\circ$ for propane at 1000 K.

(2)   *25 points.*

Imagine that 1 mol of an ideal gas, the system, is initially at 500 K and has $C_V = 10 \text{ J K}^{-1}$.

i)   It is heated by a further 200 K at constant volume. Calculate q, w, ΔU for this process. *Clearly state any extra results or relations you use in your work.*

ii)   Explain qualitatively whether you would expect q to be different if the gas had been heated by 200 K at constant pressure, and why.

(3)   *10 points.*

i)   What was the Joule experiment designed to test? [A description of the apparatus or the results is *not asked for*]

ii)   The Joule-Thompson coefficient $\mu = (\partial T/\partial p)_H$ is about 0.25 K atm^{-1} for N_2 at 298 K. If N_2 initially at 298 K and 200 atm is expanded through a small nozzle and leaves at 1 atm, estimate the approximate temperature of the N_2 [you may neglect any variation of μ with temperature].

(4)   *30 points*

Consider one mole of ideal gas, the system, initially at 200 K and $3 \times 10^5 \text{ Pa}$ and with $C_p = 25 \text{ J K}^{-1}$. It expands reversibly and adiabatically until the pressure is $1 \times 10^5 \text{ Pa}$. Calculate q, ΔU, w and ΔH for the system. You may assume that pV^γ is constant along an adiabat. *Clearly state any extra results or relations you use in your work.*

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 information: $R = 8.314$ J K^{-1} mol^{-1} 1 atm = 101325 Pa $dU = dq + dw$

$dS = dq/T$ $H = U + pV$ $G = H - TS$ $A = U - TS$

Carnot efficiency is $(T_h - T_c)/T_h$

1.   *30 points*

Consider the following Carnot cycle
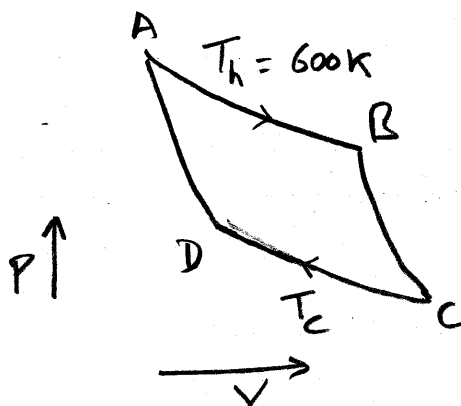
i)   In step A→B 150 J of heat were absorbed, and 70 J of work were obtained from the engine ($w = -70$ J). What is the efficiency of the engine?

ii)   How much heat is rejected at the lower temperature?

iii)   What is the lower temperature?

iv)   What is ΔS for step D→A?

2.   *35 points*

A perfect gas is expanded reversibly and isothermally (so $dU = 0$) from V_1 to V_2.

i)   Use the First Law to show $dq = pdV$ here.

ii)   Thus obtain dS, and integrate this to find ΔS.

iii) For this expansion, does the disorder of the molecules increase or decrease?

iv)   If instead the isothermal expansion from V_1 to V_2 had been carried out irreversibly, what could you say about ΔS?

3.   *35 points*

The boiling temperature of methanol, the system, is 337 K and at this temperature the enthalpy of vaporization is 35 kJ mol^{-1}.

i)   What is ΔS for vaporization at 337 K?

ii)   What is ΔS for the surroundings at 337 K?

iii) What is ΔG for the system at 337 K?

iv)   What can you say about ΔG for the system for vaporization at 340 K?

v)   What can you say about ΔS for the universe for vaporization at 340 K?

EXAM 4
21 November 1994

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 information: $R = 8.314$ J K^{-1} mol^{-1} $N_A = 6.022 \times 10^{23}$ mol^{-1} $p^\circ = 10^5$ Pa.

$$dU = dq + dw \qquad H = U + pV \qquad A = U - TS$$

$$G = H - TS \qquad d \ln K/d\, T^{-1} = -\Delta H/R$$

$$k = A \exp(-E_a/RT) \qquad \Delta_r G = \Delta G^\circ + RT \ln Q$$

(1)   *20 points.*

By expressing dA in terms of small changes of V and T, find a general expression for $(\partial S/\partial V)_T$ in terms of p, V and T only.

Use this expression to find ΔS for the isothermal expansion of one mole of a non-ideal gas from an initial volume V_1 to final pressure V_2, where the equation of state is $p(V-a) = RT$ for one mole.
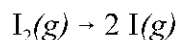
(2)   *20 points.*

Imagine the reaction $A \rightarrow 3B$, with a rate law $v = k[A]^{1/2}$.

i)   What is the order of the reaction?

ii)   Initially there is pure A at concentration $[A]_0$. Derive an expression for [A] as a function of time t.

iii)   What is the half-life for this reaction?

(3)   *30 points.*

Initially pure I_2 vapor in a container at 700 K and 1000 Pa partially dissociates according to the reaction

$$I_2(g) \rightarrow 2\, I(g)$$

until equilibrium is reached and the partial pressure of I_2 is 600 Pa.

i)   What is the degree of dissociation α for I_2?

ii)   What is the equilibrium constant (treat the gases ideally)?

iii)   What is ΔG° for the reaction?

iv)   Given that $\Delta S^\circ = 20$ J K^{-1} mol^{-1}, find ΔH° and predict the value of the equilibrium constant at 600 K (you may assume ΔH° and ΔS° are constant over 650-700 K).
[If you have no answer to part (iii), assume that $\Delta G^\circ = -3$ kJ mol^{-1}].

v)   If some of the iodine, I_2 or I, were removed from the container would α increase, decrease or stay the same, and why? [No reason = no credit]

(4)   *20 points.*

Consider the reaction mechanism for the overall reaction A → 2B.

1.   A → 2X   rate constant = k_1
2.   2X → A   rate constant = k_2
3.   X → B rate constant = k_3
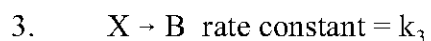
i)   What are the molecularities of step 2 and step 3?

ii)   If step 3 is slow and 1 and 2 are fast, what rate law is implied [*HINT* think of the formation of product]?

iii)   If step 1 is slow and 2 and 3 are fast, what rate law is implied?