EXAM 1

26 September 1997

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 S_2 and O_2 are 0.064 and 0.032 kg mol^{-1}, respectively.

(1)   *20 points*
a)   A system absorbed 500 J of heat while raising a weight in the surroundings. The weight's potential energy increased by 200 J. What was ΔU for the *system*?
b)   It was found that 0.02 m^3 of an ideal gas at 298 K and 101325 Pa had a mass of 0.059 kg. What is the molar mass? Be sure to give units.

(2)   *30 points*
The equation of state for 1 mole of an imaginary gas is

$$p = \frac{RT}{V-b} - \frac{a}{V^3}$$

a)   Work out an expression for dp/dV. What is the numerical value of this quantity at the critical point?
b)   For "pV" work, dw $= -$pdV. Derive an expression for the work done, w, during the reversible isothermal compression of this gas from V_1 to V_2 at a temperature T.

(3)   *30 points*
The average kinetic energy ε of ideal gas molecules is given by $\varepsilon = 3k_B T/2$. Consider gaseous samples of S_2 and O_2 at the same T.
a)   What is the ratio of the average kinetic energies of S_2 and O_2 molecules at 300 K?
b)   What is the ratio of the root mean square molecular speeds of S_2 and O_2 molecules at 300 K?
c)   What is the ratio of the root mean square molecular speeds of O_2 molecules at 300 and 600 K?

(4)   *20 points*
a)   1 mol of a real gas is confined at a pressure $p = 10^8$ Pa and at a temperature $T = 180$ K. Its critical properties are $p_c = 3.33 \times 10^7$ Pa, $V_c = 4 \times 10^{-5}$ m^3 and $T_c = 150$ K. Use the principle of corresponding states, together with the information on the figure, to estimate Z and hence the volume V.
b)   Generally, for a real gas, Z$>$1 at very high pressures, Z$<$1 at intermediate pressures, and Z$\approx$1 at very low pressures. At the microscopic level, explain these three observations.

EXAM 2

24 October 1997

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 <u>*brief justification or explanation.*</u>
<u>*Give units for all quantities!*</u>   ***YOUR NAME*** _____

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

$\gamma = C_p/C_V$ $C_p - C_V = nR$ (ideal gas) $dU = dq + dw$ $dS = dq_{rev}/T$

$H = U + pV$ $G = H - TS$ $A = U - TS$

(1)   *25 points*

1 mole of methanol (the system) is evaporated reversibly and isothermally at the boiling temperature 330 K at a constant pressure of 101325 Pa. Treat the vapor as an ideal gas and neglect the volume of the liquid. ΔH for this process is 80 kJ mol^{-1}. Find the seven quantities q, w, ΔU, ΔS for the system, surroundings and universe, and ΔG for this system. Clearly state any results you rely on, and show your work. If instead the evaporation had been spontaneous, how would ΔS_{uni} and ΔG have been different?

(2)   *25 points*

Given the following information:

Species	$\Delta_f H_{298}/\text{kJ mol}^{-1}$	$C_p/\text{J mol}^{-1}$
$H_2(g)$	0	0.1 T
$O_2(g)$	0	0.1 T
$H_2O(g)$	-400	0.2 T
$H_2O_2(g)$	-350	0.4 T

i) Find ΔH at 298 K for the reaction $2 H_2O_2(g) \rightarrow 2 H_2O(g) + O_2(g)$.
ii) Deduce $\Delta_f H$ for $H_2O_2(g)$ at 2000 K.

(3)   *25 points*

Starting with the definitions of C_p and H and the result that

$$\left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial U}{\partial V}\right)_T + C_V$$

show that for any material

$$C_p - C_V = \left(\frac{\partial V}{\partial T}\right)_p \left(p + \left(\frac{\partial U}{\partial V}\right)_T\right)$$

(4)   *25 points*

1 mol of ideal gas expands reversibly and adiabatically from 0.1 m³ to 0.2 m³ and its pressure drops from 10^5 Pa to 4×10^4 Pa. You may assume that along an adiabat pV^γ is constant. Calculate ΔH.

EXAM 3

21 November 1997

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 <u>brief justification</u> or explanation.

<u>Give units for all quantities</u>! **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} $\gamma = C_p/C_V$

$C_p - C_V = nR$ $dU = dq + dw$ $dS = dq/T$ $H = U + pV$ $G = H - TS$ $A = U - TS$

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(1) *30 points*

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

ii) Hence find a general expression for $(\partial U/\partial V)_T$ in terms of p, V and T, and use this to prove that $(\partial U/\partial V)_T = 0$ for an ideal gas. *HINT: start with U in terms of A, S and T.*

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(2) *40 points*

Methane sulfonic acid dissociates in water:

CH_3SO_3H *(aq)* $\rightleftharpoons$ $CH_3SO_3^-$ *(aq)* $+ H^+$*(aq)*

with equilibrium constant $K_a = 0.01$ at 298 K. Assuming the solutions are ideal,

i) Find the degree of dissociation of an initially 0.02 M solution of CH_3SO_3H, and the pH at equilibrium.

ii) Calculate the reaction Gibbs function when $[CH_3SO_3H] = 0.001$ M, $[H^+] = 0.001$ M and $[CH_3SO_3^-] = 0.002$ M. What is the corresponding direction of spontaneous reaction? *Show work.*
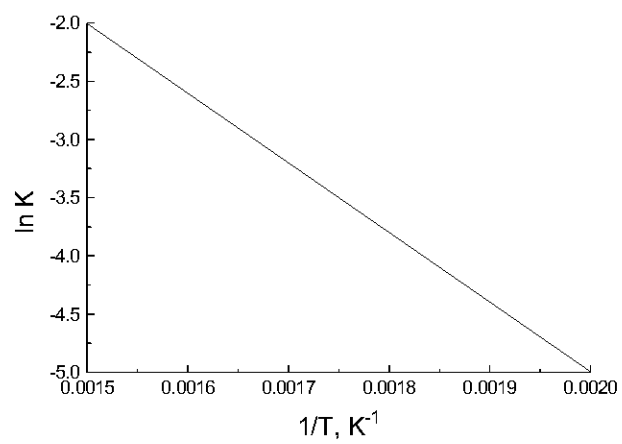
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(3) *30 points*

i) Starting from the Gibbs-Helmholtz equation,

$$\frac{d(\Delta G/T)}{dT} = -\frac{\Delta H}{T^2}$$

ΔG in terms of ln K and the assumption that ΔH is independent of temperature, prove that d ln K/d (1/T) = $-\Delta H/R$.

ii) From the graph, estimate ΔH and ΔS.

iii) Deduce ΔG at 298 K.

EXAM 4

5 December 1997

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

$C_p - C_V = nR$ $dU = dq + dw$ $dS = dq/T$ $H = U + pV$ $G = H - TS$ $A = U - TS$

$k = A \exp(-E_a/RT)$

(1)   *30 points*

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

i)   What is the order of this reaction and what are the units of k?

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

iii)   Hence derive an expression for the half-life of the reaction.
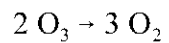
(2)   *40 points*

Consider the following proposed mechanism for enzyme kinetics where a substrate S is converted to product P in the presence of an enzyme E. ES represents an enzyme-substrate complex, and at all times $[ES] + [E] = [E]_0$, where $[E]_0$ is the initial enzyme concentration. You may assume that [ES] is in a steady state.

$$E + S \rightarrow ES \qquad \text{rate constant } k_1$$
$$ES \rightarrow E + S \qquad \text{rate constant } k_2$$
$$ES \rightarrow E + P \qquad \text{rate constant } k_3$$

i) Write out an expression for d[ES]/dt and combine it with the above relation between [ES], [E] and $[E]_0$ to derive an expression for the rate of formation of product v in terms of $[E]_0$, [S] and elementary rate constants.

ii) What are the limiting reaction orders for this mechanism when [S] is (a) very small, and (b) very large?

iii) Suggest what quantities you would plot to obtain a linear graph from a set of ([S],v) measurements, and prove that it would be linear. Explain how would you derive the two constants $A = (k_2 + k_3)/k_1$ and $B = k_3[E]_0$ from your graph.

(3)   *30 points*

Derive the rate law for the thermal decomposition of ozone whose overall reaction is

$$2\,O_3 \rightarrow 3\,O_2$$

on the basis of the following mechanism:

$$O_3 \rightarrow O + O_2 \qquad \text{rate constant } k_1$$

$$O + O_2 \rightarrow O_3 \qquad \text{rate constant } k_2$$

$$O + O_3 \rightarrow 2\,O_2 \qquad \text{rate constant } k_3$$

You may assume that [O] is in a steady state.