1) At 25°C the molar volume of CO_2 is 23,920 cm^3 at 101.3 kPa and 7878 cm^3 at 303.9 kPa. Assume that the gas follows the van der Waals equation with $a = 0.364\ m^6\ Pa\ mol^{-1}$ and $b = 4.27 \times 10^{-5}\ m^3\ mol^{-1}$. Calculate ΔU, q and w for the isothermal expansion of CO_2 from 303.9 to 101.3 kPa (17%)

2) The saturated vapour pressures of benzene and toluene are both given by the equation,

$$\log_{10}(P^\circ/Pa) = \frac{-0.05223A}{T} + B$$

where T is absolute temperature and A and B have the following values:

	A	B
Benzene	32295 K	9.7795
Toluene	39198 K	10.4549

Assuming that mixtures of benzene and toluene form ideal solutions, calculate the molar percentage of benzene in (a) a mixture which boils at 97°C under an external pressure of 1.013×10^5 Pa, and (b) the initial condensate formed on distilling this mixture. (16%)

3) A surface is half-covered by a gas when the pressure is 1 bar. The simple Langmuir isotherm applies:
(a) What is the adsorption equilibrium constant K/bar^{-1}?
(b) What pressures give 75%, 90%, 99%, 99.9% coverage?
(c) What coverage is given by pressures of 0.1 bar, 0.5 bar, 1000 bar? (17%)

4) The electromotive force of the cell

$$Zn\,|\,ZnCl_2\ (0.05\ mol\ dm^{-3})\,|\,AgCl(s),\ Ag$$

is 1.015 V at 298 K and the temperature coefficient of its electromotive force is $-4.92 \times 10^{-4}\ V K^{-1}$. Write down the equation for the reaction occurring when the cell is allowed to discharge and calculate the changes in (a) Gibbs energy, (b) entropy, and (c) enthalpy attending this reaction at 298 K. (17%)

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5) The rate constant for the thermal decomposition of ethylamine,

$$C_2H_5NH_2 \longrightarrow C_2H_4 + NH_3$$

is $1.57 \times 10^{-3}\ s^{-1}$ at 500°C. (a) Calculate the mean life and half-life for this reaction. (b) In an experiment at constant volume the initial pressure is 35 torr of ethylamine. Calculate the pressure in the vessel at 30 min. (17%)

6) Derive the integrated rate equation for an irreversible reaction of stoichiometry $2A + B \longrightarrow Z$, the rate being proportional to $[A]^2[B]$ and the reactants present in stoichiometric proportions; take the initial concentration of A as $2a_0$ and that of B as a_0. Obtain an expression for the half-life of the reaction. (16%)