CHEM 233 – Physical Chemistry

Class Test **Tuesday 8 May 2007**

Time Allowed: 60 minutes

Instructions: Answer **both questions.**
Questions 1 and 2 are worth **equal marks**.

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1. (a) Standard atmospheric pressure is 101.325 kPa. Given that R = 8.314 J K^{-1} mol^{-1}, calculate the value of the gas constant in L atm K^{-1} mol^{-1}.

(b) The acceleration due to gravity at the Earth's surface is 9.81 m s^{-2}. Calculate the height of a water barometer at standard atmospheric pressure and 4 °C. [Assume that the density of water at 4 °C is 1.000 g ml^{-1}.]

(c) Standard atmospheric pressure is 760 Torr and R = 8.314 J K^{-1} mol^{-1}.
In an experiment to measure the molar mass of a gas, 500 cm^3 of the gas was confined in a glass vessel. The pressure was 304 Torr at 25 °C and the mass of the gas was 134 mg.
Assuming perfect gas behaviour, what is the molar mass of the gas?
Suggest what the gas might be.

(d) The van der Waals equation of state is

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

(i) What is the physical meaning of each of the van der Waals parameters a and b?

(ii) Explain the assumptions of the kinetic model of gases (which leads to the perfect gas equation) that are overcome by the van der Waals equation.

(iii) Give a typical value (including units) for each of a and b.

2. (a) Distinguish clearly between the terms:

(i) reaction **rate** and **rate constant**

(ii) **order** and **molecularity**

(iii) **differential rate law** and **integrated rate law**

(b) The thermal decomposition of gaseous acetaldehyde (CH_3CHO) at temperatures around 800 K is closely described by the equation:

$$CH_3CHO \rightarrow CH_4 + CO$$

A mechanism has been proposed which accounts for the above stoichiometry and predicts that the observed order of the reaction should be $\frac{3}{2}$ with respect to acetaldehyde.

Describe how you would prove, experimentally, that the above order of reaction is valid and, also, how you would determine the **rate constant** for the reaction as well as the two Arrhenius parameters **activation energy** and **frequency** (or **pre-exponential**) **factor**.

In your description you should include: a description of an appropriate experimental technique; details of the measurements you would make; any equations you would use to test experimental data; an indication of how you would proceed to calculate the required kinetic parameters.

The Table on the following page from Atkins' *Physical Chemistry* may be useful.

Table 25.3 Integrated rate laws

Order	Reaction	Rate law*	$t_{1/2}$
0	$A \rightarrow P$	$v = k$ $kt = x$ for $0 \leq x \leq [A]_0$	$\frac{[A]_0}{2k}$
1	$A \rightarrow P$	$v = k[A]$ $kt = \ln \frac{[A]_0}{[A]_0 - x}$	$\frac{\ln 2}{k}$
2	$A \rightarrow P$	$v = k[A]^2$ $kt = \frac{x}{[A]_0([A]_0 - x)}$	$\frac{1}{k[A]_0}$
	$A + B \rightarrow P$	$v = k[A][B]$ $kt = \frac{1}{[B]_0 - [A]_0} \ln \frac{[A]_0([B]_0 - x)}{([A]_0 - x)[B]_0}$	
	$A + 2B \rightarrow P$	$v = k[A][B]$ $kt = \frac{1}{[B]_0 - 2[A]_0} \ln \frac{[A]_0([B]_0 - 2x)}{([A]_0 - x)[B]_0}$	
	$A \rightarrow P$ with autocatalysis	$v = k[A][P]$ $kt = \frac{1}{[A]_0 + [P]_0} \ln \frac{[A]_0([P]_0 + x)}{([A]_0 - x)[P]_0}$	
3	$A + 2B \rightarrow P$	$v = k[A][B]^2$ $kt = \frac{2x}{(2[A]_0 - [B]_0)([B]_0 - 2x)[B]_0} + \frac{1}{(2[A]_0 - [B]_0)^2} \ln \frac{[A]_0([B]_0 - 2x)}{([A]_0 - x)[B]_0}$	
$n \geq 2$	$A \rightarrow P$	$v = k[A]^n$ $kt = \frac{1}{n-1}\left\{\frac{1}{([A]_0 - x)^{n-1}} - \frac{1}{[A]_0^{n-1}}\right\}$	$\frac{2^{n-1} - 1}{(n-1)k[A]_0^{n-1}}$

*$x = [P]$, and $v = dx/dt$.