

CHEM 233 – Physical Chemistry

Class Test

Tuesday 8 May 2007

Time Allowed: 60 minutes

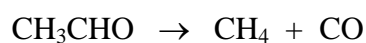
Instructions: Answer **both** questions.
Questions 1 and 2 are worth **equal** marks.

1. (a) Standard atmospheric pressure is 101.325 kPa. Given that $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, calculate the value of the gas constant in $\text{L atm K}^{-1} \text{ mol}^{-1}$.
- (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 $4 \text{ }^\circ\text{C}$. [Assume that the density of water at $4 \text{ }^\circ\text{C}$ is 1.000 g ml^{-1} .]
- (c) Standard atmospheric pressure is 760 Torr and $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$. 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 $25 \text{ }^\circ\text{C}$ 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:



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 $v = dx/dt$.