

## CHEM 233 – Physical Chemistry

Class Test

Wednesday 29 April 2009

Time Allowed: 60 minutes

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

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1. (a) Americans still use the Fahrenheit (F) temperature scale. It is related to the Celsius scale by

$$\theta_{\text{Celsius}}/^{\circ}\text{C} = (5/9)(\theta_{\text{Fahrenheit}}/^{\circ}\text{F} - 32)$$

- (i) Express  $\theta_{\text{Fahrenheit}}$  as a function of absolute temperature  $T$  in K.  
(ii) What is the temperature of absolute zero ( $T = 0$ ) on the Fahrenheit scale?  
(iii) What is the temperature in  $^{\circ}\text{F}$  at which water boils (at 1 atm)?

[Useful information:  $0\text{ }^{\circ}\text{C} = 273.15\text{ K}$ ]

- (b) “Hot air rises.”  
Use your knowledge of gases to give a (simple) scientific explanation of this common phrase.
- (c) In an experiment to measure the molar mass of a gas, a (pure) sample of it was confined in a steel vessel of volume  $2.43\text{ dm}^3$ . The pressure was  $25.4\text{ lb in}^{-2}$  at  $16.8\text{ }^{\circ}\text{C}$ , and the mass of the gas was measured to be  $0.00498\text{ kg}$ . Assuming perfect gas behaviour, what is the molar mass of the gas? Suggest a possibility for what the gas could be.

[Useful information:  $1\text{ atm} = 14.70\text{ lb in}^{-2}$ ;  $R = 8.314\text{ J K}^{-1}\text{ mol}^{-1}$ ]

- (d) The van der Waals equation of state is

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

It may be shown that this leads to  $V_c = 3b$ ,  $p_c = a/(27b^2)$  and  $T_c = (8a)/(27bR)$ , where these quantities are critical (molar) volume, critical pressure and critical temperature, respectively.

- (i) Give your understanding of the term ‘critical temperature’.
- (ii) Show that in terms of so-called reduced variables, which are  $p_r = p/p_c$ ,  $V_r = V_m/V_c$  and  $T_r = T/T_c$ , the van der Waals equation is

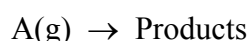
$$p_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2}$$

- (iii) What is remarkable about the result in (ii)?

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) For a decomposition reaction of the type



it may be shown that the half-life,  $\tau_{1/2}$ , of A is given by the expression

$$\tau_{1/2} = \frac{2^{n-1} - 1}{(n-1)k[A]_0^{n-1}}$$

Here  $n$  is the order of the reaction (where  $n \neq 1$ ),  $k$  is the rate constant and  $[A]_0$  is the initial concentration of A. The following data have been reported for the thermal decomposition of a gaseous organic compound, A:

| $[A]_0$ *             | At $T = 650$ K<br>$\tau_{1/2}/s$ | At $T = 720$ K<br>$\tau_{1/2}/s$ |
|-----------------------|----------------------------------|----------------------------------|
| $1.00 \times 10^{18}$ | 360                              | 37.9                             |
| $2.00 \times 10^{18}$ | 255                              | 26.8                             |
| $3.00 \times 10^{18}$ | 208                              | 21.9                             |
| $4.00 \times 10^{18}$ | 180                              | 18.9                             |

(\* **all** values of  $[A]_0$  are given in molecules /  $\text{cm}^3$ )

- (i) Using a graphical method, or otherwise, find the observed **order of reaction**.
- (ii) Calculate the **rate constant** for the decomposition process at 650 K. What are the units of your value?
- (iii) Calculate the apparent **activation energy** of the reaction.
- (iv) How would you determine the **pre-exponential** (or **frequency**) **factor**? [NB. No calculation is required in this part.]

[Data:  $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ]