

Advanced Placement Credits Test 2008 Module Template

1.	Module Code:	CM1131
2.	Module Title:	BASIC PHYSICAL CHEMISTRY
3.	Modular Credits [MC]:	4
4.	Module Description:	This module covers equations of state of ideal and real gases, kinetic theory of gases, laws of thermodynamics, and some aspects of chemical kinetics.
5.	Module Content/Syllabus: (to include topics to be covered)	<p>1. Properties of gases: Gas laws (Boyle, Charles, Dalton, ideal gas); deviation from ideal behavior; various types of intermolecular interactions and their importance; the compression factor; the critical phenomenon; the van der Waals equation; the Principles of Corresponding States; other equations of state.</p> <p>2. The first law of thermodynamics (Part I): Scope of thermodynamics; basic terms in thermodynamics; the first law of thermodynamics and its applications; internal energy, enthalpy, heat capacity and their inter-relationship; reversible versus irreversible processes; various types of processes (isothermal, isobaric, isochoric, adiabatic).</p> <p>3. Thermochemistry: Enthalpy change of a reaction; the Law of Lavoisier and Laplace; the Hess' law; standard enthalpy of formation; standard enthalpy of combustion; group additivity method of determining enthalpy of formation and heat capacity; temperature dependence of reaction enthalpy.</p> <p>4. The first law of thermodynamics (Part II): Exact differentials and some important mathematical tools; the Joule experiment; the Joule-Thomson effect and Joule-Thomson coefficient; the inversion temperature; liquefaction of gases.</p> <p>5. The second law of thermodynamics: Thermodynamics and spontaneity; the second law; efficiency of heat engine; the Carnot cycle; the Carnot theorem; power plants; entropy and entropy change; measurements of entropy; how to achieve low</p>

		<p>temperature; criteria for spontaneous process; Clausius inequality; Helmholtz energy and Gibbs energy; Gibbs energy change of a reaction.</p> <p>6. Chemical kinetics: Measurements of reaction rates; determination of rate laws; differential and integration methods; various types of rate laws; accounting for the rate laws; steady-state approximation; proposal of reaction mechanisms; the collision theory of reaction rates; the activated complex theory of reaction rates.</p>
6.	<p>Tutorial/Assignment Sample Questions (you may attach the Qns as an appendix to this document)</p>	See attached.
7.	<p>Recommended Textbooks/Readings:</p>	<p>Physical Chemistry, Peter Atkins and Julio de Paula</p> <p>Physical Chemistry, Thomas Engel and Philip Reid</p>
8.	<p>Exam Format: (please indicate the duration and assessment format, e.g. MCQ, Short-answer Qns, Essay Qns)</p>	<p>(i) Duration: 2 hours</p> <p>(ii) Assessment Format: 4 questions</p>
9.	<p>Sample of Exam Questions: (you may attach the Qns as an appendix to this document)</p>	See attached.

Tutorial Session 1

- (a) Find an expression for the Boyle temperature of a gas obeying the following equation of state.

$$V_m = (RT/p) + b - (a/RT^2)$$

where a and b are constants associated with a particular gas.

- (b) A certain amount of nitrogen gas occupies a volume of 1.00 dm^3 at 223 K and 800 bar . Determine the volume of the same amount of nitrogen gas at 373 K and 200 bar using the compression factor for nitrogen. The Z value is 1.95 at 223 K and 800 bar , and 1.10 at 373 K and 200 bar .
- (c) The critical temperature and critical pressure of nitrogen are 126.3 K and 33.54 atm , respectively, while those of ethane are 305.4 K and 48.2 atm , respectively. (i) Which gas has the smaller van der Waals constant b ? (ii) Which gas has the smaller van der Waals constant a ? (c) Which has the larger critical volume? (d) Which gas behaves more ideally at 300 K and 10 atm ?
- (d) The intermolecular forces in X are considerably larger than those in Y . Which of the following properties is not expected to be larger for X than for Y ? Show your reasoning.
- (i) The critical temperature;
 - (ii) The normal boiling point;
 - (iii) The temperature at which the vapor pressure is 0.5 bar ;
 - (iv) The molar enthalpy of vaporization (i.e. the heat required to vaporize one mole of the liquid at constant pressure);
 - (v) The vapor pressure at 298 K .

NATIONAL UNIVERSITY OF SINGAPORE

ADVANCED PLACEMENT TEST

CM1131 BASIC PHYSICAL CHEMISTRY

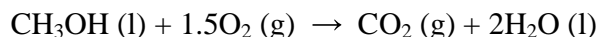
JULY 2007

INSTRUCTIONS TO CANDIDATES:

1. This is a closed book test.
2. This test paper contains **FIVE** (5) questions and comprises **FOUR** (4) pages.
3. Answer **ANY FOUR** questions.
4. Answer each question beginning on a **FRESH** page of the answer book.

Question 1

When one mole of methanol is burnt at 298 K under a constant volume condition, 726.55 kJ of heat is evolved.



- (a) What is the heat change if the reaction is carried out under a constant pressure condition?
(8 marks)
- (b) The standard enthalpies of formation of liquid water and gaseous carbon dioxide are -285.83 and -393.51 kJ mol^{-1} , respectively, at 298 K. What is the standard enthalpy of formation of liquid methanol?
(8 marks)
- (c) What is the standard enthalpy of formation of gaseous methanol at 298 K? The enthalpy of vaporization of methanol at 298 K is 35.27 kJ mol^{-1} .
(9 marks)

Gas constant $R = 8.314$ $\text{J K}^{-1} \text{mol}^{-1}$

Question 2 (25 marks)

One mole of ammonia (assumed to be an ideal gas) initially at 298 K and 1 bar is heated at constant pressure until its volume has doubled. Calculate q , w , ΔU , ΔH , and ΔS of the process. The heat capacity of ammonia at constant pressure is given by the expression:

$$C_{p,m}/\text{J K}^{-1} \text{mol}^{-1} = 25.895 + 0.03299T$$

Gas constant $R = 8.314$ $\text{J K}^{-1} \text{mol}^{-1}$

Question 3

Answer the following parts:

- (a) Explain why the entropy of vaporization of water ($109 \text{ J K}^{-1} \text{ mol}^{-1}$) is much larger than those of other liquids (about $85 \text{ J K}^{-1} \text{ mol}^{-1}$). (8 marks)
- (b) Explain why the molar heat capacity at constant pressure ($C_{p,m}$) of a gas is larger than its molar heat capacity at constant volume ($C_{v,m}$). (8 marks)
- (c) Zn is to be allowed to react with dilute sulfuric acid in (i) an open flask and (ii) a stoppered flask. Explain in which flask more heat will be evolved. (9 marks)

Question 4

- (a) A gaseous bubble with a diameter of 1 cm at the bottom of MacRitchie Reservoir, where the temperature is 5°C and the pressure is 3 atm, rises to the surface, where the temperature is 25°C and the pressure is 1 atm. Estimate the diameter of the bubble when it reaches the surface. (Ignore the presence of water vapor in the bubble and assume the ideal behavior for the gas inside the bubble). (10 marks)
- (b) To determine the molecular weight, the gas from the bubbles was collected. Its density as a function of pressure at 0°C was investigated. The following data were obtained:
- | | | | |
|--|--------|--------|--------|
| Pressure (atm): | 0.200 | 0.500 | 0.800 |
| Density ($\text{g} \cdot \text{liter}^{-1}$) | 0.2796 | 0.7080 | 1.1476 |
- Determine the molecular weight of the gas.
(Given $R = 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 0.08206 \text{ liter} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$) (10 marks)
- (c) Assume the gas behavior can be described by the following equation of state for non-ideal gases:
$$P = [RT / (V_m - b)] - a / V_m$$
where a and b are constants distinct from zero and V_m is the molar volume. Discuss if this gas has a critical point. (5 marks)

Question 5

The reaction of $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$ is one of the well-studied gaseous reactions. Before 1967, the following mechanism was generally accepted:



In 1967, Sullian showed that the reaction probably proceeds by **Mechanism II**:



- (a) Obtain the rate law for $d[\text{HI}]/dt$ predicted by **Mechanism I**. (3 marks)
- (b) Use the steady state approximation to derive the rate law for $d[\text{HI}]/dt$ from **Mechanism II**. (7 marks)
- (c) Under the assumption that reactions (1) and (2) in **Mechanism II** comprise an equilibrium with \mathbf{K} being the equilibrium constant, find the corresponding rate law for $d[\text{HI}]/dt$. Under what conditions do the results of (b) and (c) agree? (5 marks)
- (d) By producing I atoms photochemically in known concentration it is possible to measure \mathbf{k}_3 for reaction (3) in **Mechanism II**. The following data were obtained from experiments:
- | | | |
|--|--------------------|-------------------|
| T (K) | 417.9 | 520.1 |
| \mathbf{k}_3 ($\text{liter}^2 \text{mole}^{-2} \text{sec}^{-1}$) | 1.12×10^5 | 4.0×10^5 |
- where \mathbf{k}_3 is defined with reference to $-d[\text{H}_2]/dt$. Calculate the activation energy for reaction (3).
(Given $R = 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 0.08206 \text{ liter} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$) (10 marks)

End of Paper