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RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES

B.Sc. (Honors) Degree in Chemistry / B.Sc. (Joint major) Degree in Chemistry and Physics / B.Sc. (General) Degree in Applied Sciences
Third Year - Semester I Examination – September/ October 2019

CHE 3120 – CALCULATIONS IN CHEMISTRY

Time: One (01) hour

Answer **only Two (02)** questions.
Symbols have their usual meaning.

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1. a) Prove $$C_P - C_V = \left(\frac{\partial P}{\partial T}\right)_V \left\{V - \left(\frac{\partial H}{\partial P}\right)_T\right\}$$

Hints: $C_P = \left(\frac{\partial H}{\partial T}\right)_p$ $\quad C_V = \left(\frac{\partial U}{\partial T}\right)_V$

$U = H - PV$ and $H = f(P, T)$

Note: C_p and C_v are defined as thermal capacities at constant pressure and volume respectively.

(50 marks)

b) The probability of a molecule with mass m in a gas at temperature T has speed v given by the Maxwell-Boltzmann distribution,

$$f(v) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2\, e^{-mv^2/2kt}$$

where k is the Boltzmann's constant. Find the average speed,

$$\bar{v} = \int_0^\infty v\, f(v)dv$$

(50 marks)

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2. a) If pressure, volume and temperature of one mole of a gas are related as

$$\left(P + \frac{a}{V^2}\right) V = RT$$

show that,

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T + 1 = 0$$

(50 marks)

b) A slightly imperfect gas obeys the Van der Waals equation of state,

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

Find expressions for the work done by the gas in expanding reversibly from volume V_1 to volume V_2 at

i. constant pressure
ii. constant temperature

assuming a and b are constants.

(50 marks)

3. a) The Clausius-Clapeyron equation for liquid-vapor equilibrium is

$$\frac{d \ln p}{dT} = \frac{\Delta H_{vap}}{RT^2}$$

If the enthalpy of vaporization, ΔH_{vap} is constant in the temperature range T_1 to T_2 show, by integrating both sides of the equation with respect to T, that

$$\ln\left(\frac{p_2}{p_1}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

(50 marks)

where $p_1 = p(T_1)$ and $p_2 = p(T_2)$.

b) If $Z = \log(e^x + e^y)$

show that $\left(\frac{\partial Z}{\partial x}\right)_y + \left(\frac{\partial Z}{\partial y}\right)_x = 1$ (50 marks)

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