

## SOUTH EASTERN KENYA UNIVERSITY

## UNIVERSITY EXAMINATIONS 2016/2017

## SECOND SEMESTER EXAMINATION FOR THE DEGREES OF BACHELOR OF EDUCATION (SCIENCE) AND BACHELOR OF SCIENCE (CHEMISTRY)

## SCH 303: THERMODYNAMICS II AND PHASE EQUILIBRIA

DATE: 13 TH APRIL, 2017
TIME: 1.30-3.30 P.M

## INSTRUCTIONS TO CANDIDATES

(a) Answer question One and any other Two questions
(b) Question 1 carries $\mathbf{3 0}$ marks while the other questions carry 20 marks each
(c) Illustrate your answers with well label diagrams where applicable

## Constants

$R=0.0820575(\mathrm{~L} \mathrm{~atm}) /(\mathrm{mol} \mathrm{K}) ; 8.314 \mathrm{Jmol}^{-1} \mathrm{~K}^{-1} ; 0.08314 \mathrm{Lbarmol}^{-1} \mathrm{~K}^{-1}, 8.314 \mathrm{M}^{3} \mathrm{~Pa} /(\mathrm{Kmol})$ Boltzmann's constant $(\mathrm{k})=1.381 \times 10^{-23} \mathrm{JK}^{-1}$
$\mathrm{C}_{\mathrm{v}}=3 / 2 \mathrm{R} ; \mathrm{C}_{\mathrm{p}}=5 / 2 \mathrm{R}$
Question 1 (30 marks)
A). Define the second law of thermodynamics in terms of:
i). Clausius statement
ii). Kelvin planck statement
iii). Entropy
b). Sketch well labeled graphs illustrating the second law of thermodynamics based on:
[4 marks]
i). Temperature versus volume
ii). Temperature versus entropy
c). Fill the table for $\Delta \mathrm{H}, \Delta \mathrm{S}$ and $\Delta \mathrm{G}^{\mathrm{o}}$ on spontaneity.
[6 marks]

| $\Delta \mathrm{H}$ | $\Delta \mathrm{S}$ | $\Delta \mathrm{G}^{\mathrm{O}}$ | Result |
| :--- | :--- | :--- | :--- |
| + | + | + |  |
| + | + | - |  |
| - | + | - |  |
| - | - | + |  |
| - | - | - |  |
| + | - | + |  |

d). Predict the nature of $\Delta \mathrm{S}$ whether positive or negative for the systems below taking place at constant temperature. Explain the reason.
$\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \rightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{g})$
$\mathrm{Ag}^{+}(\mathrm{aq})+\mathrm{Cl}^{-}(\mathrm{aq}) \rightarrow \mathrm{AgCl}(\mathrm{s})$
$\mathrm{N}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{NO}(\mathrm{g})$
e). Give $\partial \mathbf{u}=\mathrm{T} \partial \mathrm{S}-\mathrm{P} \partial \mathrm{V}$, show that the entropy change $(\Delta \mathrm{S})$ for an ideal gas is;
[5 marks] $\Delta \mathrm{S} / \mathrm{C}_{\mathrm{v}}=\ln \mathrm{T}_{2} / \mathrm{T}_{1}+(\gamma-1) \ln \left(\mathrm{V}_{2} / \mathrm{V}_{1}\right)$
f). The vapour pressure of ice at 268 K is 2.965 atm , determine the value for its vapour pressure at 273 K.if the heat sublimation of ice is $52370 \mathrm{j} / \mathrm{mol}$.

## Question 2 (20 marks)

a). An ideal carnot engine with efficiency $\eta=0.4$ operates using 500 moles of an ideal diatomic gas as the working substance. During isothermal expansion stage, the pressure of the gas decreases to half the maximum pressure on the cycle. At the end of the adiabatic expansion stage the pressure is $9 \times 10^{5}$ Pascals and its volume is $2 \mathrm{M}^{3}$.
i). Sketch the carnot engine cycle and label all the stages involved.
[4 marks]
i). Calculate the heat at the isothermal compression stage.
[4 marks]
ii). Heat absorbed from the high temperature reservoir.
iii). Calculate the entropy changes at each stage.

## Question 3 (20 marks)

a). If $\partial u=\partial q+\partial w$, proof the carnot heat pump coefficient:
$\mathrm{CoP}=\mathrm{T}_{\mathrm{H}} /\left(\mathrm{T}_{\mathrm{H}}-\mathrm{T}_{\mathrm{C}}\right)$
b). Calculate the standard entropy change $\Delta \mathrm{S}$ for the reaction.

$$
2 \mathrm{H}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g})
$$

$$
\mathrm{S}^{\mathrm{o}} \mathrm{~J} /(\mathrm{Kmol})
$$

$\mathrm{H}_{2} \mathrm{O}(\mathrm{g})$
188.7
$\mathrm{H}_{2}(\mathrm{~g})$
131
$\mathrm{O}_{2}(\mathrm{~g})$
205
c). Solve for the value of $\Delta \mathrm{G}$ change in the reaction;
$2 \mathrm{CO}(\mathrm{g})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{CO}_{2}(\mathrm{~g})$
Given;
pressure (atm) at $25^{\circ} \mathrm{C} \quad \Delta \mathrm{G}^{\mathrm{o}} \mathrm{kJ} / \mathrm{mol}$
$\mathrm{O}_{2}$ 0.50

0
CO
0.30
137.2
$\mathrm{CO}_{2}$
0.45
394.4

## Question 4 (20 marks)

a). Find $\Delta \mathrm{G}^{\circ}$ for the reaction at $25^{\circ} \mathrm{C}$ and $1000^{\circ} \mathrm{C}$. Explain whether the reaction is spontaneous or nonspontaneous, hence determine the temperature of spontaneity.

|  | $\Delta \mathrm{H}^{\mathrm{o}} \mathrm{kJ} / \mathrm{mol}$ | $\mathrm{S}^{\mathrm{o} J} /(\mathrm{Kmol})$ |
| :--- | :--- | ---: |
| $\mathrm{CaCO}_{3}$ | -1207 | 92.9 |
| CaO | 92.9 | 38.2 |
| $\mathrm{CO}_{2}$ | -394 | 214 |

b). Derive the equation of Helmholtz energy (A), if;

$$
\mathrm{A}=\mathrm{U}-\mathrm{TS}
$$

c). If $\partial \mathrm{E}=\mathrm{T} \partial \mathrm{S}-\mathrm{P} \partial \mathrm{V}$, show that;

## Question 5 (20 marks)

a). Derive the Gibbs-duhem equation, if $\mathrm{G}=\mathrm{U}+\mathrm{PV}-\mathrm{TS}$
b). Calculate the value of the equilibrium constant $\left(\mathrm{K}_{\mathrm{p}}\right)$ at $25^{\circ} \mathrm{C}$ for the reaction below. [5 marks]

$$
2 \mathrm{NO}_{2}(\mathrm{~g}) \rightleftharpoons \mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g})
$$

$$
\Delta \mathrm{G}_{\mathrm{f}}^{\mathrm{o}} \mathrm{~kJ} / \mathrm{mol}
$$

$$
\begin{array}{ll}
\mathrm{NO}_{2}(\mathrm{~g}) & 51.3 \\
\mathrm{~N}_{2} \mathrm{O}_{4}(\mathrm{~g}) & 99.8
\end{array}
$$

c). State four assumptions of the Gibbs phase rule.
d. Proof that $\Delta \mathrm{S}=\mathrm{C}_{\mathrm{p}} \ln \left(\mathrm{T}_{2} / \mathrm{T}_{1}\right)$ for the entropy change when one mole of a gas undergoes a reversible expansion at constant pressure ( P 1 ) from $\mathrm{P}_{1}, \mathrm{~V}_{1}, \mathrm{~T}_{1}$ to $\mathrm{P}_{1}, \mathrm{~V}_{2}, \mathrm{~T}_{2}$
[6 marks]

