Loughborough University

Energetics and Equilibria 1

22CMA105

Semester 2 22/23 | In-Person Exam paper

This examination is to take place in-person at a central University venue under exam conditions. The standard length of time for this paper is **2 hours**.

You will not be able to leave the exam hall for the first 30 or final 15 minutes of your exam. Your invigilator will collect your exam paper when you have finished.

<u>Help during the exam</u>

Invigilators are not able to answer queries about the content of your exam paper. Instead, please make a note of your query in your answer script to be considered during the marking process.

If you feel unwell, please raise your hand so that an invigilator can assist you.

You may use a calculator for this exam. It must comply with the University's Calculator Policy for In-Person exams, in particular that it must not be able to transmit or receive information (e.g. mobile devices and smart watches are **not** allowed).

List of Common Constants (note that not all of these will necessarily need to be used in your answers)

Planck constant, $h = 6.626 \times 10^{-34}$ J s

Mass of electron, $m_e = 9.109 \times 10^{-31}$ kg

Atomic mass unit, $u = 1.66054 \times 10^{-27}$ kg

Avogadro constant, $N_A = 6.022 \times 10^{23}$ mol^{-1}

Boltzmann constant, $k = 1.380 \times 10^{-23}$ J K^{-1}

Speed of light, $c = 2.998 \times 10^{8}$ m s^{-1}

gas constant, $R = 8.314$ J K^{-1} mol^{-1}

acceleration due to gravity, $g = 9.80665$ m s^{-2}

0 °C = 273.15 K

1 atm = 760 mmHg = 760 Torr = 101325 N m^{-2}

Answer **ALL** questions

1. Advice: read the full question before starting to answer it.

a) Calculate the lattice energy of rutile, TiO_2, using the Born-Landé equation. The equation and key data are provided below.

$$\Delta U = \frac{-N_A M|z_+||z_-|e^2}{4\pi\varepsilon_o r}\left(1 - \frac{1}{n}\right)$$

Internuclear separation, r = 2.05 Å = 2.05×10^{-10} m;

e: charge on an electron (1.602×10^{-19} C);

ε_o: permittivity of a vacuum (8.854×10^{-12} Fm^{-1});

N_A: Avagadro's constant (6.022×10^{23});

n(O) = 7; n(Ti) = 9;

M = 2.408

[5 marks]

b) The answer you should have got in part (a) is larger than for many of the examples studied during the course. Discuss why this is the case. [3 marks]

c) Construct a Born-Haber cycle for the formation of TiO_2 from the elements in their standard states. Use the data given below to calculate the ΔH_{LATT} for this system. Outline any assumptions you have made and show full working.

$\Delta H_f(TiO_2,s)$ = –944 $kJmol^{-1}$; $\Delta H_a(Ti,g)$ = 471 $kJmol^{-1}$

$IE_1(Ti,g)$ = 659 $kJmol^{-1}$; $IE_2(Ti,g)$ = 1310 $kJmol^{-1}$

$IE_3(Ti,g)$ = 2653 $kJmol^{-1}$; $IE_4(Ti,g)$ = 4175 $kJmol^{-1}$

$\Delta H_{EA1}(O,g)$ = –141 $kJmol^{-1}$; $\Delta H_{EA2}(O,g)$ = 798 $kJmol^{-1}$;

$\Delta H_a(O,g)$ = 249 $kJmol^{-1}$.

[10 marks]

d) Explain why there is a difference in the values obtained in parts (a) and (c).

[2 marks]

Continued…

e) Given the bond enthalpy data below (all in kJ mol^{-1}), show numerically and explain why oxygen exists as a diatomic (O=O), while sufur is a solid comprising S_8 molecules with single S–S bonds.

B(O–O) = 144; B(S–S) = 226; B(O=O) = 498; B(S=S) = 425.

[5 marks]

2. Note, the following Relative Atomic Masses are required for this question: Na 22.99; K 39.10; Rb 85.47; Cs 132.91; Ni 58.69; Cl 35.45; C 12.01; O 16.00; Al 26.98; S 32.06; H 1.01; N 14.007.

a) "Alums", of formula $MAl(SO_4)_2 \cdot 12\,H_2O$ (where M is a Group1 cation Na^+, K^+, Rb^+ or Cs^+), are all known compounds. An unidentified sample of weight 2.500 g was dissolved in 50 ml of water and then 17.0 ml of a 0.75 M (i.e. mol l^{-1}) solution of EDTA added.

After addition of Fast Sulphon Black F (FSB) indicator, a standardised 0.4 M copper solution was titrated into this solution until the end point. This occurred after 18.24 ml of the copper solution had been added.

Identify the cation M in this case, fully showing your working. [7 marks]

b) List, with brief explanation in each case, four key features that would make a compound suitable as a primary standard for redox titrations. [4 marks]

c) A solid sample of nickel dichloride dihydrate, $NiCl_2 \cdot 2H_2O$, weighing 4.231 g was dissolved in 50 ml of water. A 17.5 ml sample of the resulting solution was treated with an excess of dimethylglyoxime and a base.

Describe, with full explanation, the reaction in terms of observations (colour changes, etc.) and the mass of any precipitate. [5 marks]

d) The reaction of HCl with manganese dioxide, MnO_2, provides a useful means of generating chlorine gas in the laboratory. Derive a balanced equation for this reaction, explaining your reasoning and indicating which elements are undergoing redox. [4 marks]

Continued…

e) For the following reactions, determine whether or not a redox process is occurring, taking care to highlight which elements are undergoing redox, to add any further classification of reaction type (e.g. comproportionation, etc.) and, in the case of (ii), balance the equation.

(i) $IF_5 + AsF_5 \rightarrow [IF_4][AsF_6]$

(ii) $Pb + PbO_2 + H_2SO_4 \rightarrow PbSO_4 + H_2O$

(iii) $2\ H_2O_2 \rightarrow O_2 + 2\ H_2O$

[5 marks]

3\. a) What are the properties of a gas and how do they relate to kinetic energy?

[3 marks]

b) (i) A 300 L cylinder of hydrogen gas has a pressure of 350 atm. If it is compressed to 200 L, what will be the resulting pressure? [3 marks]

(ii) How many moles of hydrogen is stored in a 300 L cylinder of hydrogen at a pressure of 350 atm and a temperature of 25 °C? [7 marks]

c) The Clausius-Clapeyron equation is as follows:

$$ln\left(\frac{P_f}{P_i}\right) = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_f} - \frac{1}{T_i}\right)$$

(i) Define the terms. [4 marks]

(ii) The vapour pressure of a substance is 15 torr at 300 K. Calculate the vapour pressure at 310 K if the enthalpy of vaporisation is 24 kJ mol^{-1} and comment on your answer. [6 marks]

d) Using the Gibbs phase rule, calculate the number of degrees of freedom of hydrogen in a pressurised cylinder. Comment on your answer. [2 marks]

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