Name ______________________________________

MBSE Core Knowledge Exam

Tuesday, May 31, 2022
9:00 am – noon

Instructions:

- You have three hours in which to complete the exam.
- Answer all four questions—they all carry the same weight, they all require approximately the same effort and length of answer.
- Be sure to read each question carefully, and please ask for clarification if you don't understand the meaning.
- Please start your answer to each question on a new page.
- Include all the details of your thought process, along with any sketches, graphs, equations, and derivations needed to support your arguments. Be sure to label all sketches and graphs clearly, define all variables that you use, and clearly state all relevant assumptions.
- Your answers must contain only your own work. You may not consult any outside sources (written, spoken, or electronic) during the exam.
- You may use a calculator, only to crunch numbers.
- You will find some potentially useful tables at the end.

Good luck!

Question 1

(a) Structure, bonding, property relationship.

TiO and YN both adopt the rock salt structure. YN is an electrical insulator whereas TiO is an electrical conductor.

(i) Please explain the reason behind the difference in electrical properties. Sketch diagrams to aid your explanation.

(ii) Based on your answer from (a), what is the nature of bonding in TiO vs. YN?

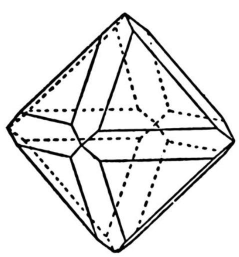
(iii) How would you describe the rock salt structure using the space sharing polyhedra model?

(iv) What interstitial site(s) is (are) vacant in this structure for doping?

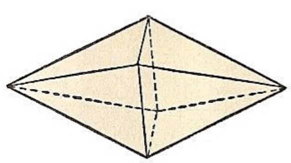
(b) Crystal symmetry.

Based on symmetry, to which crystal system does each of the following single crystals belong? Please explain your reasoning.

(i)



(ii)



(c) Bravais lattices.

Body centered cubic (BCC) is one of the Bravais lattices for the cubic crystal system. Other possible centering within the cubic system includes primitive and face-centered lattices. Why doesn't a base-centered cubic lattice exist? Please provide two reasons. Sketch diagrams to aid your explanation.

Question 2

Structure, energy, properties.

In the context of the mechanical behavior of metal alloys, describe (in detail, and with reasons) the characteristics of the ideal precipitate. Note that "ideal" will depend on the intended application of the material. Your answer should address relevant aspects of structure (crystallography) and thermodynamics (energy and stability).

Question 3

Energy, structure, properties.

Consider the following three phenomena:

(i) It is possible to make ice cream by placing the ingredients in a sealed Ziploc® bag, placing that bag in a larger Ziploc® bag that contains ice and salt, sealing the outer bag, and then shaking this vigorously.

(ii) An aircraft descending through clouds encounters turbulence as it enters the cloud layer.

(iii) When protracted frost is predicted, almond farmers in the Central Valley will flood the ground in their orchards, so that there is a significant amount of standing water under the trees.

There is a common factor underlying these three phenomena. Use your core knowledge and understanding to carefully explain the phenomena, and to identify what they have in common.

Question 4

Electrochemistry.

Many important processes of interest in materials science involve electrically charged species. They play central roles in electrolysis, fuel cells, batteries, and corrosion, among others, and in each of these cases materials design and/or selection is crucial to real-world performance.

(a) We begin with a simple electrolytic cell, consisting of two electrodes in water, spaced a finite distance apart, with the objective being to produce hydrogen and/or oxygen gas. A constant potential difference (voltage) is applied to the electrodes, and its magnitude is large enough to form both gases, one at each electrode. The temperature T and pressure p are fixed.

In water at finite temperature there is always some small amount of dissociation of water molecules into ionic species:

$$H_2O \longleftrightarrow H^+ + OH^- \tag{4.1}$$

Because of the applied potential difference, the H^+ ions tend to migrate to the negative electrode, where they are reduced to form H_2 gas:

$$2H^+ + 2e^- \longrightarrow H_2 \tag{4.2}$$

In addition, the OH^- ions tend to migrate to the positive electrode, where they are oxidized to form O_2 gas:

$$4OH^- \longrightarrow 2H_2O + O_2 + 4e^- \tag{4.3}$$

In answering the questions below, be sure to write down and explain the relevant equations before inserting numbers, document the meanings of the variables, and explain the reasons for the signs of the energy flows. Table 1 gives some molar thermodynamic data that may be useful, and these constants may also be useful: $R = 8.315\ \mathrm{J\,mol^{-1}K^{-1}}$ (molar gas constant), $1\ \mathrm{eV} = 1.602 \times 10^{-19}$ J (electron volt), $N_A = 6.022 \times 10^{23}\ \mathrm{mol^{-1}}$ (the Avogadro constant), $e = 1.602 \times 10^{-19}$ C (proton charge).

Substance (form)	$\Delta_f \hat{H}$ (kJ)	$\hat{S}$ (J/K)	$\hat{C}_p$ (J/K)	$\hat{V}$ (cm^3)
H_2 (g)	0	130.68	28.82	
H (g)	219.97	114.71	20.78	
H^+ (aq)	0	0	0	
H_2O (l)	−285.83	69.91	75.29	18.068
H_2O (g)	−241.82	188.83	33.58	
O_2 (g)	0	205.14	29.38	
O_2 (aq)	−11.7	110.9		
OH^- (aq)	−229.99	−10.75	−148.5	

Table 1: Molar thermodynamic data for water and related species [a caret denotes a molar quantity]. The values are given for $T = 298.15$ K and $p = 10^5$ Pa. The forms listed are liquid (l), gas (g), and aqueous solution (aq). For differences ($\Delta_f \hat{H}$) the reference state for liquid and gas forms is the component elements in their most-stable pure states. For ions in aqueous solution, the concentration is 1 mole per kilogram of water, and the reference is H^+, arbitrarily assigned the value 0 for all thermodynamic quantities.

For each mole of O_2 produced,

(i) find the chemical equation for the overall reaction,

(ii) find the amount of heat input Q to the system from the thermal reservoir (T = 298.15 K),

(iii) find the amount of pressure-volume (pV) work input W_{pV} to the system from the pressure reservoir ($p = 10^5$ Pa),

(iv) find the electrical work input W_{elect} required,

(v) find the change in the internal energy of the system,

(vi) find the change in the Gibbs free energy of the system,

(vii) find the amount of charge, in Coulombs, transported through the external circuit.

Also:

Make a schematic sketch of the energy flows into and out of the system, specifying the magnitude (absolute value) of each (based on values that you computed above) and indicating clearly its direction (into or out of the system) and its identification (heat, pV work, electrical work, …).

(b) The processes occurring in a rechargeable battery are similar, but the current flows in opposite directions when charging and discharging. As an example, a common type of Li-ion battery has, in the discharged state, a graphite electrode, a $LiCoO_2$ electrode, and an organic-liquid electrolyte with some kind of dissolved lithium salt so that it contains Li^+ ions. On charging, Li^+ ions are formed at the $LiCoO_2$ electrode (depleting it of lithium) and consumed at the other electrode, with Li atoms intercalated in the graphite. The process is reversed on discharge, and the half-cell reactions are:

$$CoO_2 + Li^+ + e^- \longleftrightarrow LiCoO_2 \quad \text{and} \quad LiC_6 \longleftrightarrow C_6 + Li^+ + e^- \tag{4.4}$$

with discharge shown as the forward reactions in both cases.

Development of solid-state electrolyte materials is a high priority, as the liquid electrolytes are flammable and cannot safely be used with Li metal electrodes (which yield higher energy density than graphite) because of formation of Li dendrites that eventually cause internal short circuits, leading to fire and/or explosion.

(i) Briefly compare and contrast the mechanisms for ionic conduction in liquid and solid electrolytes.
Which would you expect to have greater conductivity at room temperature?

(ii) What sorts of crystal-structure features might you expect to be associated with high ionic conductivity?
Why?

(iii) Some competing battery technologies use other metal ions as the internally transported species. What sorts of properties of metal ions would you expect to be associated with high conductivity in a solid electrolyte?
Why?

Useful Information

Crystal system	Characteristic/ defining symmetry	Viewing directions			Point group / crystal class (full symbol)
		1st letter	*2nd letter*	*3rd letter*	
Triclinic	1-fold symmetry	1 or $\bar{1}$			1 or $\bar{1}$
Monoclinic	One 2-fold (diad)	*b (c)*			$2,\ m,\ \frac{2}{m}$
Orthorhombic	Three 2-folds (diad)	*a*	*b*	*c*	$222,\ 2mm,\ \frac{2}{m}\frac{2}{m}\frac{2}{m}$
Tetragonal	One 4-fold (tetrad)	*c*	*a*	[110]	$4,\ \bar{4},\ \frac{4}{m}$ $422,\ 4mm,\ \bar{4}2m,\ \frac{4}{m}\frac{2}{m}\frac{2}{m}$
Trigonal	One 3-fold (triad)	*c*	*a*	[210]	$3,\ \bar{3}$ $32,\ 3m,\ \bar{3}\frac{2}{m}$
Hexagonal	One 6-fold (hexad)	*c*	*a*	[210]	$6,\ \bar{6},\ \frac{6}{m}$ $622,\ 6mm,\ \bar{6}2m,\ \frac{6}{m}\frac{2}{m}\frac{2}{m}$
Cubic	Four 3-folds (triad)	*a*	[111]	[110]	$23,\ \frac{2}{m}\bar{3}$ $432,\ \bar{4}3m,\ \frac{4}{m}\bar{3}\frac{2}{m}$

Periodic Table of Elements

1 H 1.00794																	2 He 4.002602
3 Li 6.941	4 Be 9.012182											5 B 10.811	C 12.0107	7 N 14.00674	8 O 15.9994	9 F 18.9984032	10 Ne 20.1797
11 Na 22.989770	12 Mg 24.3050											13 Al 26.581538	14 Si 28.0855	15 P 30.973761	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc 44.955910	22 Ti 47.867	23 V 50.9415	24 Cr 51.9961	25 Mn 54.938049	26 Fe 55.845	27 Co 58.933200	28 Ni 58.6534	29 Cu 63.545	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.92160	34 Se 78.96	35 Br 79.504	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.90585	40 Zr 91.224	41 Nb 92.90638	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.90550	46 Pd 106.42	47 Ag 196.56655	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.760	52 Te 127.60	53 I 126.90447	54 Xe 131.29
55 Cs 132.90545	56 Ba 137.327	57 La 138.9055	72 Hf 178.49	73 Ta 180.94.79	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.217	78 Pt 195.078	79 Au 196.56655	80 Hg 200.59	81 Tl 204.3833	82 Pb 207.2	83 Bi 208.58038	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 (269)	111 (272)	112 (277)		114 (289) (287)		116 (289)		118 (293)

58 Ce 140.116	59 Pr 140.50765	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.964	64 Gd 157.25	65 Tb 158.92534	66 Dy 162.50	67 Ho 164.93032	68 Er 167.26	69 Tm 168.93421	70 Yb 173.04	71 Lu 174.967
90 Th 232.0381	91 Pa 231.035888	92 U 238.0289	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)