Materials Science and Engineering
PhD Qualifying Exam

WRITTEN EXAM:
Tuesday, May 20th, 2025
9:00AM-1:00PM, 15 Saint Mary's Street, Room 105

- **NO ELECTRONIC DEVICES** (smartphone, iPad, smartwatch) permitted • Calculators and a ruler are allowed.
- CLOSED BOOK. Only the notes indicated below will be allowed.

INSTRUCTIONS:

1) Write your **EXAM NUMBER** on every sheet of paper

1) Write clearly and legibly as the exam may be scanned to faculty for grading.

2) **Answer 5 out of 6 questions** completely in the three required sections below:

Section I:

- **Problems 1 and/or 2:** Electrical, Optical and Magnetic Properties of Materials (MS 577/PY 543, Swan/Hu)
    - CLOSED BOOK, ONE ONE-SIDED FORMULA SHEET

Section II: **Problems 3 and/or 4:** Thermodynamics and Statistical Mechanics (MS 505, Pal)

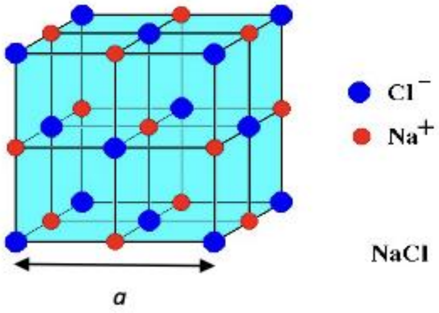
- CLOSED BOOK, ONE ONE-SIDED FORMULA SHEET

Section III: **Problems 5 and/or 6**: Kinetic Processes in Materials (MS 503, Basu)

- CLOSED BOOK, NO NOTES

Both question 1 and 2 pertain to NaCl. Use the information given here that is relevant for the question you solve.

NaCl has a rock-salt structure where the *conventional unit cell* is shown. The ionic radii are Na: r=0.09 nm and Cl: r=0.18 nm. The masses are $M_{Na} = 22.99\, u$, $M_{Cl} = 35.45\, u$ respectively. Assume the x-ray $\frac{10}{18}$ scattering form factors for Na^{+} and Cl^{-} are having a fixed ratio $f^{\underline{NA}}$ of f_{Cl} = for all G vectors (simplification).



1. **Crystal structure and scattering.**

    a) Real space: What is the lattice structure? What is the size of the lattice parameter a?

    b) Reciprocal space: What G vectors (i.e., what hkl's) are allowed? What is the size of the reciprocal unit cell?

    c) Consider NaCl powder x-ray diffraction using x-rays with wavelength $\lambda = 0.15406\, nm$. Give the hkl's for the first 5 peaks, the angular position of the scattering angle 2θ, and the calculated intensity of the peaks, not including the geometric factor from the geometry of the setup, i.e., $I_{hkl} \propto |S_{hkl}|2M_{hkl}$. Use $S_{hkl} = S_{lattice,hkl} \cdot S_{basis,hkl}$. Draw the $I(2\theta)$ result approximately to scale.

2. **Phonons and heat capacity.**

    a) What is the crystal structure, and how many atoms per primitive unit cell does NaCl have?

    b) Heat capacity: The Debye temperature for NaCl is 281 K. What is the value of the heat capacity at room temperature (300K)? Either give the answer in units of k_B per unit cell, or $k_{mol}{}^{\underline{B}N\underline{A}}{}_{e}$. Draw the heat capacity as a function of temperature to scale, with the temperature and the heat capacity values marked on the axes. What is the functional form of the dispersion at low T? What if any is the contribution from electrons to the heat capacity?

c) For a primitive unit cell containing N atoms in 3 dimensions, there are always 3 acoustic modes and 3(N-1) optical branches. How many acoustic, optical branches for NaCl? Draw a schematic of the phonon dispersion in the ΓX direction and label transverse acoustic (TA) and longitudinal acoustic (LA) branches. Similar for optical modes, if applicable. What is the zone π boundary k-vector (in units of)? The Y-axis for the phonon dispersion has the unit of energy

a

($\hbar\omega$). What is the approximate max energy of the phonon dispersion, any branch? (how do you know?)

Materials Ph.D. Qualifying Examination
(allowed 1-page open notes, double-sided)

SECTION I (Thermodynamics)

1. The elements A and B are both solid at 1273 K. They also form two stoichiometric solid compounds A_2B and AB_2 at 1273 K. System A-B does not contain any solid solutions. A has an immeasurably small vapor pressure at 1273 K, and for the equilibrium B(s) = B (g)

$$\Delta G^{\circ} = 187{,}220 - 108.8T(K) \quad (J)$$

The vapor pressure of B exerted by an equilibrated A_2B-AB_2 mixture is given by

$$\log p\,(atm) = -\frac{11{,}242}{T(K)} + 6.53$$

and the vapor pressure of B exerted by an equilibrated A-A_2B mixture is given by

$$\log p\,(atm) = -\frac{12{,}603}{T(K)} + 6.9$$

Calculate the standard Gibbs free energies of formation of A_2B and AB_2.

2 a. Derive a relationship starting from the first law that describes the rate of change of temperature of an adiabatic dry parcel of air as it moves up or down in the atmosphere; assume that air behaves as an ideal gas. Given g (acceleration due to gravity) is 9.8 m/s^2 and C_p for dry air is 1,005 J/kg-K, can you calculate the expected temperature change of the parcel of air when it moves up 3 km? Discuss the implications of the rate of change of temperature with height if the parcel of air is saturated with water vapor. **(75 points)**

b. Suppose a 30 °C air parcel at the ground level has a dew point temperature of 14 °C, and it is rising through the atmosphere. Estimate the altitude at which the clouds begin to form if the dew point drops by 2 °C/km. **(25 points)**

May 2025 MSE Qualifier Questions: MS 503

Closed book, NO additional notes

Some physical constants and kinetic formulas that may or may not be relevant:

Gas constant, R = 8.314 J/mole-K
Avagadro's constant, $N_{Av} = 6.023 X 10^{23}$ mole^{-1}
Plank's constant, h = $6.626 X 10^{-34}$ J-s
Boltzman's constant, k = $1.381 X 10^{-23}$ J/K
Charge of an electron, e = $-1.602 X 10^{-19}$ Coulombs

Diffusivity equations

$$J_1 = -D_1 \, {}^{\partial c_1}/_{\partial x} = -L_{11} \, {}^{\partial \mu_1}/_{\partial x}, D_1 = B_1 RT \left(1 + \frac{\partial ln\gamma_1}{\partial lnX_1}\right)$$

$$c(x,t) = {}^{S}\!\Big/\!\sqrt{4\pi Dt}\, \exp(-x^2/4Dt), \; c(x,t) = A + Berf(x/2\sqrt{Dt}),$$

$$c(x,t) = \frac{4c^0}{\pi}\sum_{i=0}^{\infty}\frac{1}{2j+1}\sin\left(\frac{(2j+1)\pi x}{l}\right)\exp\left(-\left(\frac{(2j+1)\pi}{l}\right)^2 Dt\right)$$

$$\bar{c}(t) = \frac{8c^0}{\pi^2}\sum_{i=0}^{\infty}\frac{1}{(2j+1)^2}\exp\left(-\left(\frac{(2j+1)}{l}\right)^2 Dt\right)$$

$$\text{D(vacancy mechanism)} = \gamma a^2 \nu_D p_v \exp\left(-\frac{\Delta G_m^v}{RT}\right),$$

$$\text{D(interstitial mechanism)} = \gamma a^2 \nu_D \exp\left(-\frac{\Delta G_m^i}{RT}\right),$$

Chemical reactions

For chemical reaction: aA + bB = cC + dD;

$$\frac{d[C]}{dt} = -\frac{c}{a}\frac{d[A]}{dt}$$

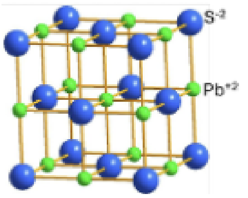
$$\exp(-\Delta G^0/RT) = \exp(-\Delta g^0/kT) = (a_C)^c (a_D)^d/(a_A)^a (a_B)^b$$

$$\text{Reaction rate} = K_f [A]^{\alpha} [B]^{\beta} - K_b [C]^{\gamma} [D]^{\delta}$$

Adsorption/desorption

adsorption rate = $k_{ad}(1-\phi)\, p_{CO}$, Desorption rate = $k_{de}\,\phi$

Problem 1.



Assume that Pb^{+2} and S^{-2} ions in PbS diffuse predominantly by the vacancy mechanism in the Pb and S sublattices in PbS, respectively. PbS has a rocksalt structure, implying cations (Pb^{+2}) and anions (S^{-2}) are arranged in an FCC structure in their own sublattices (see figure). Assume that in a PbS crystal, the shape of the pathway between a lattice Pb^{+2} ion and an adjacent Pb vacancy is identical to the pathway between a lattice S^{-2} ion and an adjacent S vacancy.

DATA: $r_{Pb2+} = 1.20$Å, $r_{S2-} = 1.84$Å

a) The predominant point defects in PbS is formed by the Frenkel reaction in the Pb sublattice. Do you expect $[V_{Pb}'']$ or $[V_S^{\cdot\cdot}]$ to be larger? Explain using all appropriate defect reactions.

b) Based on the information stated above, can you definitely expect D_{Pb} or D_S in PbS to be greater? Expain. HINT: Write the full equation for both diffusivities and consider relative values of all the terms.

c) How would you expect doping of PbS by Cs_2S to effect D_{Pb}? Write two appropriate defect incorporation reactions and justify which one is valid. DATA: $r_{Cs^+} = 1.81$Å

d) How would you expect doping of PbS by Bi_2S_3 to effect D_{Pb}? Write two appropriate defect incorporation reactions and justify which one is valid. DATA: $r_{Bi+3} = 1.02$Å

Problem 2.

a) The surface of Pt is a catalyst for many low temperature chemical reactions. Assume that each surface Pt atom is a potential site for a certain catalytic reaction. Gas phase carbon monoxide (CO) molecules are known to adsorb on surface Pt atoms effectively poisoning those sites and preventing the catalytic reaction. Assume that at most one CO molecule can adsorb on a given surface Pt atom. If the fraction of poisoned surface sites, ϕ, is defined as:

ϕ = number of CO poisoned surface sites/number of total surface sites,

show that the equilibrium value of $\phi = \frac{k_r p_{CO}}{1+p_{CO}}$, where $k_r = k_{ad}/k_{de}$ (ratio of adsorption and desorption kinetic constants) and p_{CO} is the partial pressure of CO in the atmosphere. What would a plot of ϕ versus p_{CO} look like?

b) The rate of the catalytic reaction, r_C, is proportional to the fraction of sites that have not been poisoned, with a proportionality constant of k_C. What will a plot of r_C versus p_{CO} look like?

c) Now assume that the adsorption of CO on the Pt surface is irreversible, i.e., $k_{de} = 0$. Now the fraction of poisoned sites will increase with time. For this case, **derive** an expression of ϕ as a function of time, t, in term of p_{CO} and k_{ad}. Assume that the surface of platinum is clean at the start. Show this in a plot of ϕ versus t.

d) For the case of part c), what will a plot of r_C versus t look like?