

University of Alabama System
Materials Science Ph.D. Program
Program Examination I

Organization

The Tri-Campus Ph.D. Materials Science Committee has restructured the Program Examination-1 to put the topics covered on the examination more in line with the basic information with which every practicing Materials Scientist should be familiar.

The PE-1 examination will consist of three sections: Section 1. Structures and Properties; Section 2. Characterization and Testing; and Section 3. Thermodynamics and Processing. Each examination will be limited to 2 hours and will consist of two parts, a short answer part and a more detailed essay or problem part. The use of multiple-choice answers in the short answer part should be discouraged because of possible ambiguous answers. Instead a short written answer should be required. The essay/problem portion should offer a broad choice of questions to be answered in order to accommodate students with different backgrounds.

The examination will be given approximately every September and February. Every student in the Materials Science Ph.D. Program may take this first examination without penalty should they not pass it. Every new student may also take the first examination offered after they enter the program without penalty. All students in the Materials Science Ph.D. Program will be expected to take all three sections of the examination after their first full year of graduate study in the Program and will have two attempts to pass it. Those students who do well on two of the three sections and fail one section may take just that section at the next offering. Students failing two or more sections must retake the entire examination at the next offering.

A syllabus for each of the sections is provided below for students to use in preparation for the examination and for faculty members preparing the examination. Each question should be referenced back to the syllabus in the master examination file to assure that questions do not go beyond the syllabus. Campus Coordinators will have a complete set of the required books to loan to students preparing for the examination.

A study guide for each section is also attached. These questions are largely from the first two offerings of the revised PE-1, with the exception of a few additional questions from Section 1.

While a consider number of examinations given prior to Fall 2004 are available, students should not focus on them in their preparations. The attached syllabi and examples are far more representative of the current examination.

Syllabi

Section 1. Structure and Properties of Materials

Notes

1. These examination topics are covered with varying degrees of detail in many introductory materials texts. Students are not expected to study all of these books exhaustively, but rather to master the topics, which may require reading several of them.
2. Students who have taken a course in Solid State Physics may find most of the subjects covered at a higher level in Kittel or in Ashcroft and Mermin. However, since these texts do not cover all of the topics in this examination, such students are encouraged to refer to the representative texts for completeness.
3. The two texts by Callister are very similar but are aimed at slightly different audiences. Their major differences are mainly organizational.
4. In some cases, many of the subtopics are addressed in a single chapter and, therefore, specific sections are not specified. The chapter number is given in the major headings (such as "1") and the subheadings (such as 1.1...) are labeled "---."
5. In the case that a text does not address a topic, the cell is labeled "N.A."

Representative Texts

- Call:* *Fundamentals of Materials Science and Engineering*, 2nd Ed., William. D. Callister, Jr., John Wiley and Sons, Inc., 2005, ISBN 0-471-47014-7.
- Call2:* *Materials Science and Engineering - An Introduction*, 6th Ed., William D. Callister, Jr., John Wiley and Sons, Inc., 2003, ISBN 0-471-13576-3.
- Sh:* *Introduction to Materials Science for Engineers*, 5th Ed., James F. Shackelford, Prentice-Hall, 2000, ISBN 0-13-011287-9.
- Ask:* *The Science and Engineering of Materials*, 4th Edition, Donald R Askeland and Pradeep P. Phule, Thomson Learning-Brooks/Cole, 2003, ISBN 0-534-95373-5.

Examination Topics

Topic	Reference Text			
	Call	Call2	Sh	Ask
1. Chemical Bonding	2	2	2	2
1.1. Atomic and molecular orbitals	---	---	---	---
1.2. Primary bonding	---	---	---	---
1.3. Secondary bonding	---	---	---	---
2. Basic lattice types	3	3	3	3
2.1. Bravais lattices	---	---	---	---
2.2. Miller indices	---	---	---	---
2.3. Coordination in metals	---	---	---	---
2.4. Interstitial size and location	N.A.	N.A.	N.A.	---
2.5. Relation between CN and cation/anion ratio in ceramics	---	12.2	---	---
3. Classes of materials - bond type and general structure	2	2	1.3, 2	1-2, 2
3.1. Metals	---	---	---	---
3.2. Ceramics and inorganic glasses	---	---	---	---
3.3. Semiconductors	---	---	---	---
3.4. Polymers	---	---	---	---
3.5. Composites	15.1	16.2	14 (Intro)	16 (Intro)

Topic	Reference Text			
	Call	Call2	Sh	Ask
4. Mechanical properties				
4.1. Crystal defects	5.1-5.10	4.1-4.8	4	4
4.2. Deformation and fracture (tensile stress-strain)	7.1-7.8	6.1-6.8	6.1-6.3	6-1 thru 6-4
4.3. Strengthening mechanisms	8	7	10	
4.3.1. Solid solution	---	---	---	9-4
4.3.2. Work hardening	---	---	---	7-1 thru 7-3
4.3.3. Grain refining	---	---	---	4-8
4.3.4. Precipitation hardening	11.10-11.12	11.9	---	11-1 thru 11-7
4.3.5. Dispersion hardening	15.3	16.3	---	10-1
5. Electrical properties	12	18	15	12
5.1. Classical theory of electrical conduction	---	---	---	---
5.2. Free and nearly free electron model of metals	---	---	---	---
5.3. Ionic conduction	---	---	---	---
5.4. Conduction in semiconductors	---	---	---	---
6. Thermal properties	17 ¹	19 ²	7.1, 7.3	21-1, 21-3
6.1. Lattice vibrations and phonons	---	---	---	---
6.2. Heat conduction	---	---	---	---
6.3. Heat capacity and the Debye model	---	---	---	---
6.4. Electronic conduction and Wiedemann-Franz ratio	---	---	---	---
6.5. Electronic heat capacity	---	---	---	---
7. Optical Properties	19.1-19.9	21.1-21.9	161-16.2	20-1 thru 20-3
7.1. Bandgap and photonic absorption	---	---	---	---
7.2. IR absorption in ionic materials	---	---	---	---
7.3. Polarization and dielectric function	---	---	---	---
7.4. Absorption and transmission	---	---	---	---
8. Magnetic properties	18.1-18.6	20.1-20.6	18.1-18.3	19-1 thru 19-4
8.1. Diamagnetism	---	---	---	---
8.2. Paramagnetism	---	---	---	---
8.3. Ferromagnetism	---	---	---	---
8.4. Ferrimagnetism	---	---	---	---
9. Ferroelectrics			15.4	18-10
9.1. Pyroelectrics	12.24	18.24	N.A.?	---
9.2. Piezoelectrics	12.25	18.25	15.4	---
10. Superconductors	18.12	20.11	15.3	18-4
10.1. Meissner effect	---	---	---	---
10.2. London equations	---	---	---	---
10.3. Type I and II superconductors	---	---	---	---
10.4. High T _c superconductors	---	---	---	---

¹ Exclude sections 17.3 and 17.5.

² Exclude sections 19.3 and 19.5.

Section 2. Characterization and Testing

Reference Books

Basic Materials texts:

Call *Fundamentals of Materials Science and Engineering, 2nd Ed.*, W.D. Callister or

Sh *Introduction to Materials Science for Engineers, 5th Ed.*, J.F. Shackelford

Note: Similar information may be found in later editions of Callister (or other texts)

Instrumental Methods texts:

SHN *Instrumental Method of Analysis, 5th Ed.*, D.A. Skoog, F.J. Holler, T.A. Nieman or

WMD *Instrumental Method of Analysis, 7th Ed.*, H.W. Willard, L.L. Merritt, J.A. Dean

Physical Chemistry texts:

At *Physical Chemistry, 5th Ed.*, Peter Atkins

Topics

Topic	Reference Text				
	<i>Call</i>	<i>Sh</i>	<i>SHN</i>	<i>WMD</i>	<i>At</i>
1. X-ray Diffraction	3.20	3.7	12A	13, 13.1, 13.2 ³	
2. Mechanical properties and testing	---	---	---	---	
2.1. Tensile testing including modulus of rupture	7.2, 7.3, 7.6, 7.7	6.1			
2.2. Impact testing and fracture toughness	9.2-9.8	8.1, 8.2			
2.3. Fatigue testing	9.9, 9.10	8.3			
2.4. Creep testing	9.16, 9.17	6.5			
2.5. Hardness tests	7.16	6.4			
3. Spectroscopy ⁴			6A-B, 7A-E	5-5.6	
3.1. UV-Vis			8A, 13A-B	7-7.1	17.1- 17.4
3.2. IR-FTIR-Raman			16A-16C, 18A-B	11-11.2, 12-12.1	16.1-16.7 ⁵
3.3. Optical emission					
3.4. AA (Atomic Absorption)			9A-B	9.4	
3.5. AES (Atomic Emission Spectroscopy)			10A-C	9.1, 9.2	
3.6. XRF (X-Ray Fluorescence)			12A, 12C	5.10, 13, 13.5	
3.7. XPS/ESCA/EDS/EELS/AES (Auger Emission Spectroscopy)			21A-D	5.9, 13, 13.1, 13.2, 13.7, 13.8	17.8-17.10
3.8. SIMS			21B	16.14	
3.9. NMR			19	5.8, 15-15.4	18.1-18.3
4. Surface Analysis ⁶ (Optical Microscopy, SEM, SPM, LEED)			21A-D		

³ Bragg equation

⁴ Underlying principles, information obtainable, and limitations

⁵ Exclude selection rules

Topic	Reference Text				
	<i>Call</i>	<i>Sh</i>	<i>SHN</i>	<i>WMD</i>	<i>At</i>
5. Thermal Analysis ⁷ (TGA, DSC, TG)			31A-D	25-25.5	
6. Electrical Characterization					
6.1. Conductivity measurements					
6.2. Hall measurements	12.14				
7. Molecular weight determination ⁸					
7.1. Gel permeation chromatography and size exclusion chromatograph				20.9	
7.2. Light scattering				7.11	

⁶ Underlying principles, information obtainable, and limitations

⁷ Underlying principles, information obtainable, and limitations

⁸ Underlying principles, information obtainable, what is being measured, and limitations

Section 3. Thermodynamics and Processing

References

- GR:* N. A. Gokcen and R. G. Reddy: Thermodynamics, Plenum Press, N.Y., 1996
- RA:* R. E. Reed-Hill and Reza Abbaschian: Physical Metallurgy Principles, PWS-Kent Publ. Co., Boston, 1992
- CBK:* Y. M. Chiang, D. P. Birnie III and W.D. Kingery: Physical Ceramics, John Wiley & Sons, Inc., New York, 1997
- MO:* M. Ohring: Materials Science of Thin Films- Deposition and Structure, Academic Press, New York, 2002

Syllabus

Topic	Chapter (Pages)	Reference Text
Thermodynamics		
1. Fundamentals		GR
1.1. First Law	3 (37-40)	GR
1.2. Enthalpy And Heat Capacity	3 (53-60)	GR
1.3. Thermochemistry	3 (60-67)	GR
1.4. Second Law	4 (71-78, 87)	GR
1.5. Concept of entropy	4 (79-82)	GR
1.6. Entropy Change	5 (89-93)	GR
1.7. Helmholtz and Gibbs Energies	6 (101-108)	GR
1.8. Third Law	7 (109-113, 116-117)	GR
1.9. Entropy of Supercooled liquids	7 (114-115)	GR
1.10. Gibbs Energy Change of Reactions	12 (203-215)	GR
1.11. Equilibrium constants	12 (204, 212-214, 240-244)	GR
1.12. Thermodynamic Equations	12 (215-216)	GR
1.13. Thermodynamics Tables and Compilations	12 (216-238)	GR
2. Phase Equilibria		GR
2.1. Single component systems	8 (119-120)	GR
2.2. Binary and higher order systems	8 (120-124)	GR
2.3. Phase rule	8 (133-135)	GR
2.4. Clapeyron equation	8 (119-124)	GR
2.5. Fugacity and Activity	9 (139-144)	GR
2.6. Raoult's Law	9 (144-145)	GR
2.7. Henry's Law	9 (145-149)	GR
3. Solutions		GR
3.1. Ideal Solutions	10 (151-161)	GR
3.2. Real Solutions	10 (162-172)	GR
3.3. Dilute Solutions	10 (172-173)	GR
3.4. Regular Solutions	11 (189-190)	GR
3.5. Partial and Excess Gibbs Energy	8 (130-133, 135-136), 10 (173-175), 11 (179-183)	GR
3.6. Equilibria in Gas Mixtures	12 (209-212)	GR
3.7. Complex Equilibria	12 (238-244)	GR

Topic	Chapter (Pages)	Reference Text
4. Solutions of Electrolytes		GR
4.1. Electrolytes	13 (247-256, 262-263)	GR
4.2. Temkin Rule	13 (264)	GR
4.3. Half-cell potentials	14 (267-272)	GR
4.4. Standard emf of Half-cells	14 (272-277)	GR
4.5. Cells with Solid Electrolytes	14 (280-282)	GR
4.6. Corrosion –Pourbaix diagrams	App. V (181-183)	GR
5. Phase Diagrams		GR
5.1. Binary and ternary phase diagrams	15 (285-290, 302-309)	GR
5.2. Lever Rule	15 (290-291)	GR
5.3. Gibbs Energy-composition diagrams	15 (291-298)	GR
5.4. Order-disorder phenomena	16 (330-333)	GR
5.5. Surface Tension	16 (323-325)	GR
5.6. Gibbs Adsorption	16 (325-326)	GR
5.7. Gravitational Field	16 (327-329)	GR
5.8. Electric and Magnetic Fields	16 (329-330)	GR
Materials processing fundamentals (Basic processes - applications)		
1. Solidification and Microstructure		RA
1.1. Diffusion	12 (360-364)	RA
1.1.1. Fick's laws	12 (362, 373-401)	RA
1.2. Nucleation and Growth	14, 15	RA
1.2.1. Heterogeneous nucleation	15 (495-498)	RA
1.2.2. Growth Kinetics	15 (498-509)	RA
1.2.3. Dendritic growth	14 (444-458)	RA
1.2.4. Segregation	14 (459-467)	RA
1.2.5. Porosity	14 (467-476)	RA
1.2.6. Martensitic transformations	17 (561-584)	RA
2. Powder Processing		CBK
2.1. Solid phase sintering	5 (392-428)	CBK
2.2. Hot isostatic pressing	5 (429-430)	CBK
2.3. Glass and Glass – Ceramics	5 (430-460)	CBK
2.4. Crystallization and Glass Formation	5 (431-446)	CBK
3. Deposition Processes		MO
3.1. Physical vapor deposition	3-5	MO
3.1.1. Thin Film Evaporative Processes	3 (95-140)	MO
3.1.2. Discharges. Plasmas, and Ion-Surface Interactions	4 (145-183)	MO
3.1.3. Plasma and Ion Beam Processing of Thin Films	5 (203-269)	MO
3.2. Chemical vapor deposition	6	MO
3.2.1. Thermodynamics of CVD	6.3 (287-292)	MO
3.2.2. Gas Transport	6.4 (293-302)	MO
3.2.3. Film Growth Processes	6.5 (303-312)	MO
3.2.4. Thermal CVD Processes	6.6 (312-322)	MO
3.2.5. Plasma Enhanced CVD Processes	6.7 (323-333)	MO

Examples/Study Guide

Section 1. Structure and Properties of Materials

Assorted Equations and Constants

Periodic Table of Elements																		
Periods	Groups																	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIII			IB	IIB	IIIB	IVB	VB	VIB	VII	VIII

1	1																	2
	H																	He
2	3	4											5	6	7	8	9	10
	Li	Be											B	C	N	O	F	Ne
3	11	12											13	14	15	16	17	18
	Na	Mg											Al	Si	P	S	Cl	Ar
4	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	87	88	89	104	105	106	107	108	109	110	111	112		114		116		118
	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub		Uuq		Uuh		Uuo

6		¹	58	59	60	61	62	63	64	65	66	67	68	69	70	71
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
7		²	90	91	92	93	94	95	96	97	98	99	100	101	102	103
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Part 1. Short Answer Questions

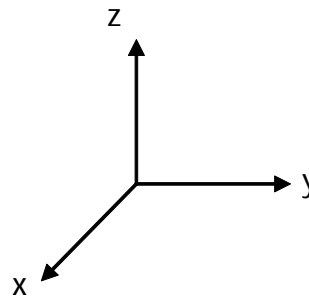
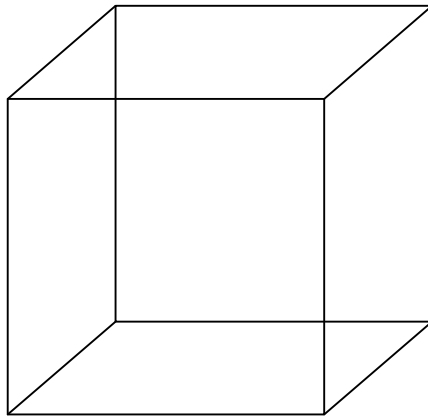
Chemical Bonding

1. Which electrons control atomic bonding?
2. Based on the periodic table, what would you anticipate the primary bond(s) would be between Ni and O? Why?
3. Describe the manner in which electrons are rearranged in metallic bonding.
4. Why do elements in the same column of the periodic table exhibit the same bonding behavior?
5. What atomic property determines the extent of ionic and covalent bonding in a compound? Relate the behavior to positions in the periodic table.
6. Describe the manner in which electrons are redistributed in ionic bonding.

Basic Lattice Types

7. What determines the coordination number in ionically bonded materials?
8. Define a unit cell.
9. What are the correct brackets to denote a family of planes in Miller indices? A specific direction?
10. What is the relationship between a crystal system and a Bravais lattice? Which has more information and what is that information?
11. Define atomic packing factor. How does it relate to density?
12. How are hexagonal close-packed (HCP) and face-centered cubic (FCC) structures related?
13. What is a unit cell and what are the lattice parameters in a unit cell?
14. Which metallic structures are close-packed?
15. What type of brackets are used for a generic plane of a given hkl (family of planes)?

16. What type of brackets are used for a generic direction of a given hkl? _____
17. There are _____ basic unit cell types, such as cubic, tetragonal et cetera.
18. In a substitutional solid solution, the solute atoms sit on a lattice site of the solvent (host) lattice. (T/F) _____
19. What is the difference in stacking in an HCP versus an FCC metallic structure?
20. What are the close-packed planes and directions in FCC and HCP metallic structures?
21. What is the close-packed direction in a BCC metallic structure?
22. How are ceramic and polymer crystal structures different from metallic crystal structures?
23. What is an interstitial?
24. What is a substitutional solid solution?
25. Draw (and label) on the unit cell below a $[\bar{1}11]$ and $(0\bar{1}2)$.



26. What is an interstitial solid solution?
27. What critical data do we need to predict the crystal structure of ceramic materials?
28. Amorphous materials (select all correct answers):
 - a. exhibit long range order
 - b. exhibit short-range order

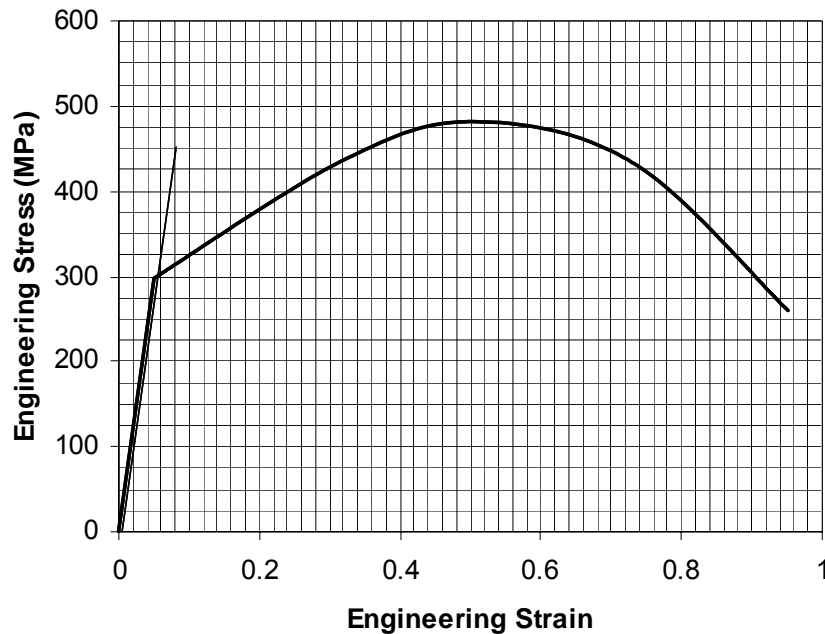
Classes of Materials

29. What is (are) the primary chemical bond(s) in ceramics?
30. Based on bonding, how are thermoset and thermoplastic polymers different?

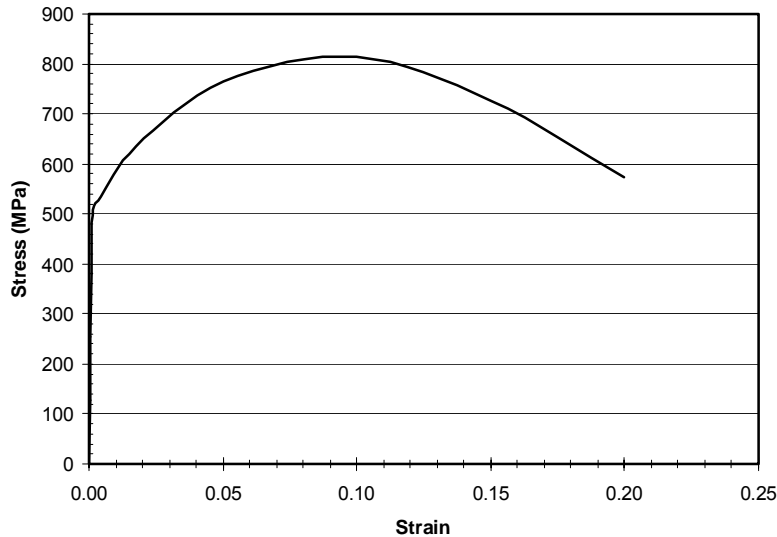
Mechanical Properties

31. During work-hardening, what happens to the strength and ductility of the material?
32. What is the physical origin of elasticity in metals and ceramics?
33. What is a vacancy? What is the temperature dependence of vacancy concentration?
34. Sketch a schematic stress strain curve for commercially pure aluminum. Label the elastic regime, plastic regime, and ultimate tensile strength.
35. Strengthening of metals depends on reducing or eliminating the motion of _____.
36. Label the following as a point, line, or planar defect:
 - a. _____ Grain boundary
 - b. _____ Vacancy
 - c. _____ Dislocation
37. When we say a material is brittle, what property that we determine from a tensile test is low?
38. Why is the stress necessary to deform a crystal significantly lower than that predicted by calculating the force necessary to simultaneously break all the bonds along a plane in a crystal?
39. How does permanent deformation occur in a crystalline solid?
40. A dislocation is a _____ defect.
41. In BCC metals, slip generally occurs:

- a. along $\langle 111 \rangle$ directions in $\{110\}$ planes
 - b. along $\langle 111 \rangle$ directions in $\{111\}$ planes
 - c. along $\langle 110 \rangle$ directions in $\{111\}$ planes
 - d. along $\langle 100 \rangle$ directions in $\{110\}$ planes
 - e. along $\langle 100 \rangle$ directions in $\{111\}$ planes
 - f. along $\langle 110 \rangle$ directions in $\{110\}$ planes
 - g. along $\langle 110 \rangle$ directions in $\{100\}$ planes
42. If the dislocation is parallel to its Burgers vector, it is a _____ dislocation.
43. If it becomes easier for a dislocation to move through a material, the strength of the materials has likely _____ (increased or decreased).
44. List four ways that a metal could be strengthened. What is the mechanism by which the strengthening occurs?
45. Sketch the relationships between (i.) % cold work and yield strength and (ii) % cold work and ductility.
46. Cold working of a metal increases the strength of the metal. What is the physical reason for this?
47. Typically as the strength of a metal increases, what happens to the ductility?
48. Describe how the mechanisms by which ceramics, metals and polymers (both thermoplastics and thermosets) plastically deform. Include in your discussion an explanation on how the deformation mechanism affects the materials ductility.
49. A round bar of aluminum with a length of 10 m and 100 mm in diameter is loaded in tension. For this material, $E = 7 \text{ GPa}$, $\sigma_y = 210 \text{ MPa}$ (0.2% offset), $\sigma_{TS} = 400 \text{ MPa}$, necking begins at $\Delta l/l = 0.4$, fracture occurs at $\epsilon = 0.9$ and the fracture stress is 300 MPa.
- a. Sketch a schematic stress-strain curve, including as much of the above information as possible.
 - b. Calculate the length of the bar immediately before failure.
 - c. Calculate the maximum load that this bar can carry without plastic deformation occurring.
50. Use the following stress-strain curve to answer questions.
- a. Calculate Young's Modulus for this material.
 - b. The strain at which this specimen begins to neck.
 - c. What is the length of the specimen, which was originally 50 mm long, just prior to fracture?
 - d. What is the load to which a 12.5 mm diameter specimen can be loaded without permanent deformation?



51. Sketch (on the same axes) a tensile stress-strain curve for a ceramic, a metal, a thermoplastic polymer, and a thermoset polymer.
52. Label the following defects as point (P), line (L), or planar (A).
 - a. Grain boundary _____
 - b. Dislocation _____
 - c. Twin _____
 - d. Vacancy _____
53. What is cold work? How cold is cold? How do you calculate %CW ? How does the formula change for rolling?
54. What happens to the structure of a metal when it is cold-worked? Think about grain shape and dislocations.
55. What happens to the properties of a metal when it is cold-worked?
56. How does annealing change the structure of cold-worked metals? How does annealing change the properties of cold-worked metals?
57. What are the stages of annealing? How do the properties change for each?
58. What is hot work?
59. What is the Hall-Petch equation? What does it say about strength and grain size?
60. In an engineering stress-strain curve below, determine the ultimate tensile strength, the yield stress, and the % elongation at failure.



Electrical Properties

61. State Matthiessen's rule.
62. Define the mobility of a charge carrier (the formula will do).
63. Write a formula for the conductivity of a semiconductor in terms of the mobilities of the charge carriers.
64. For metals, what is the effect of the following variables on resistivity?
 - a. _____ Purity
 - b. _____ Temperature
 - c. _____ Cold work
65. Derive the relationship between a material's conductivity (an intrinsic property) and the resistance (an extrinsic property)

Thermal Properties

66. Define heat capacity. (a formula will do)
67. What is the Wiedemann-Franz law? (a formula will do).
68. Define thermal conductivity. (a formula will do)
69. Define heat capacity. (a formula will do)
70. Consider the electronic contributions to the heat capacities of a metal and semiconductor. Which one would you expect to be larger? Why?
71. Sketch the dependency of thermal conductivity of ceramics as a function of temperature. Explain the physical origin of this behavior.
72. Sketch the heat capacity of a solid as a function of temperature. What is the limiting value of molar heat capacity?

Optical Properties

73. Define index of refraction. (a formula will do)
74. How is the reflectivity of a material related to its index of refraction? (a formula will do).

75. How is the index of refraction related to the dielectric constant of a material? (a formula will do)
76. Briefly explain why ruby (single crystal aluminum oxide with chromium oxide additions) is red, polycrystalline aluminum oxide is opaque, and single crystal aluminum oxide (sapphire) is clear.
77. Briefly explain why metals are opaque to electromagnetic radiation having photon energies within the visible region of the spectrum.
78. Explain the basic concepts of laser operation.

Magnetic Properties

79. The electron configuration of Fe is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$, and the electron configuration of Cu is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$. Use this information to explain why Fe is ferromagnetic and Cu is not.
80. Cobalt is a ferromagnetic material while aluminum is paramagnetic. Describe what you expect for the remanance of these materials if a magnetic field is applied to these materials, and then removed.
81. What two motions of electrons are important in determining the magnetic properties of materials?
82. Draw hysteresis loops of "hard" and "soft" magnetic materials and give an application for each.

Ferromagnets and Superconductors

83. Co, Ni and Fe exhibit ferromagnetic behavior. Explain why this is true, base on their electronic structure.
84. Consider the following materials: Label each as a ferromagnet (FM), a metallic superconductor (MS) or a ceramic superconductor (CS).

_____ $\text{YBa}_2\text{Cu}_3\text{O}_2$

_____ Nb_3Sn

_____ $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$

_____ Fe

_____ PbMo_6S_8

_____ Co

Ferroelectrics and Piezoelectrics

85. What is the difference in magnetostriction and electrostriction, and what kinds of materials exhibit these effects?
86. The Curie temperature is an important characteristic of ferroelectric and ferromagnetic materials. Define this temperature and draw a curve to represent either the dielectric constant or the magnetization versus temperature to illustrate the Curie temperature.
87. What is the difference between piezoelectricity (both direct and converse), pyroelectricity and ferroelectricity? Give an example of an application of converse piezoelectricity.
88. What is the piezoelectric effect? Give an example of an application of the use of this effect?

89. Give a definition of a ferroelectric material. Why does a ferroelectric material such as barium titanate lose its ferroelectric characteristics above its Curie temperature?

Superconductors

90. In a Type I superconductor, while in the superconducting state, is completely diamagnetic. What does this mean, and is there a name for this effect?

91. There are two classes (metallic, polymer, ceramic, plasma, etc) of materials that have been found to exhibit superconductivity. What are these two classes, and give an approximate temperature range for the highest observed superconducting temperature for each class.

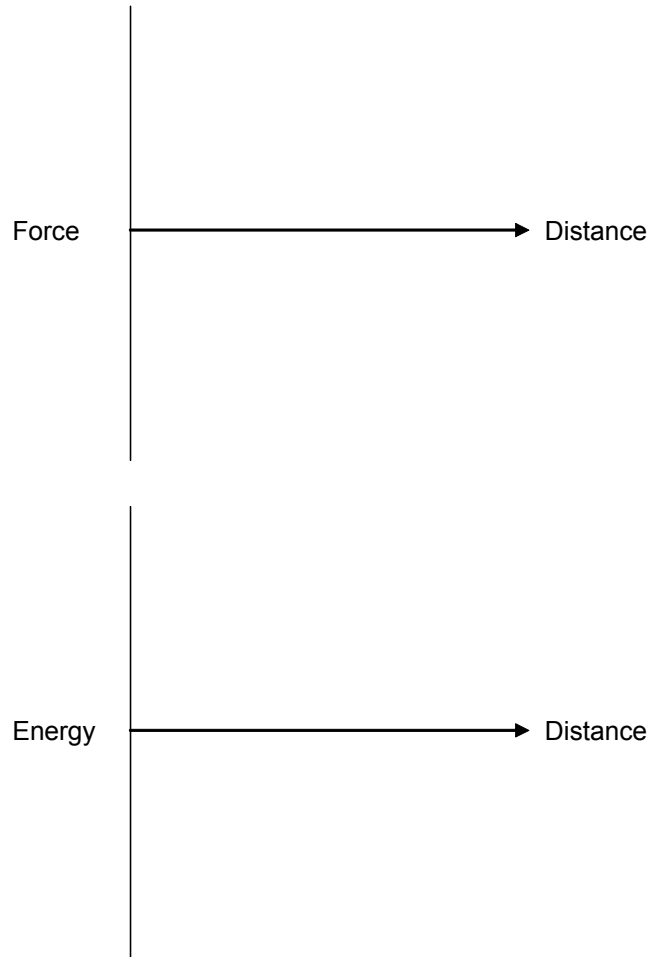
92. The critical current density for an Nb_3Sn superconductor at a temperature of 4 K and in a field of 1000 Oe is $1 \times 10^5 \text{ A/cm}^2$. What diameter Nb_3Sn wire would be required for operation as a superconductor under these conditions?

93. Draw a curve of electrical resistivity versus temperature for a normal metal and a superconducting material at temperature near absolute zero. Give an application of the use of a superconducting material.

Part 2: Essay/Problem Questions

Chemical Bonding

1. Complete the following schematic plots for a high-melting point material. Label the bond energy and the equilibrium interatomic separation. On the energy/distance plot, show (and clearly label) how a low-melting point material would behave



2. Explain how valence electron structure determines the primary bond in a material. Use Na-Cl, Si-Si, and Cu-Cu atom pairs as examples.
3. The bond energy of NaCl is 640 kJ/mol. The bond energy of MgO is 1000 kJ/mol. Which would you expect to have a higher melting point? Higher modulus? Higher thermal expansion. Explain your reasoning!
4. How can you use the periodic table and electronegativities to predict bonding?
5. Briefly explain how metallic, ionic, covalent, and secondary bonding differ in the manner in which electrons are redistributed and the relative strength of the bond (give a ranking)

Basic Lattice Types

6. Explain the difference between a crystalline and amorphous structure. Use SiO₂ as your example.
7. Derive the lattice parameter of a face-centered cubic simple metal (such as Al or Cu) in terms of the atomic radius.

8. Calculate the lattice parameters of BCC and FCC iron. The atomic radius of Fe is 0.124 nm.

Classes of Materials

9. Ceramics are generally poor electrical conductors. Based on their bonding, explain why.
10. Describe the bonding and structure in polymers. How do thermosets and thermoplastics differ?
11. Compare the four major classes of materials (ceramics, metals, polymers, and semiconductors) in terms of typical strength, ductility, elastic modulus, melting point, and thermal conductivity. For simplicity, you may use aluminum oxide, copper, polypropylene, and silicon as prototypical examples.
12. Define a composite material. List two different common ways that we classify them. List three examples of composite materials, including their classifications (your answer above), their constituents, and how they are used.

Mechanical Properties

13. Describe how the strength of an Al-4%Cu alloy changes as aging time at 160°C increases. The material was initially completely solutionized. How do the strengthening mechanisms change?
14. Describe why the theoretical and observed strengths of metals differ. Include in your answer the mechanism by which metals deform and how the presence of solute atoms affects it.
15. Slip generally occurs along close packed directions between close packed planes.
- What are the slip planes and slip directions in BCC and FCC materials?
 - Why does slip tend to occur this way?
 - What is the Burgers vector?
 - Name the three major types of perfect (or complete) dislocations.
16. Describe how the strength of an Al-4%Cu alloy changes as aging time at 160°C increases. The material was initially completely solutionized. How do the strengthening mechanisms change?
17. Discuss the changes in strength and ductility of brass as it is increasingly plastically deformed by rolling. How does the microstructure change on the levels of optical microscopy and transmission electron microscopy? Use sketches as helpful.

Electrical Properties

18. What are the three types of polarization that dielectrics may be subject to? Discuss the origin and the effect of each and tell approximately over which frequency it becomes important.
19. What is meant by an n-type and a p-type semiconductor? How do you make an intrinsic semiconductor such as pure silicon n- or p-type?
20. Describe the electron band structures at 0 K for metals, insulators, and semiconductors. Give values and standard terminology as possible.

Thermal Properties

21. Using a sketch of bonding energy as a function of distance between atoms, show how thermal expansion occurs.

22. Sketch the heat capacity of a solid as a function of temperature. What is the limiting value of molar heat capacity?
23. Sketch the dependency of thermal conductivity of ceramics as a function of temperature. Explain the physical origin of this behavior.
24. Sketch the heat capacity of a solid as a function of temperature. What is the limiting value of molar heat capacity?

Optical Properties

25. Explain how photoconductivity occurs.
26. Briefly explain why metals are opaque to electromagnetic radiation having photon energies within the visible region of the spectrum.
27. Explain the basic concepts of laser operation.

Magnetic Properties

28. Draw a hysteresis loop (B vs. H) for a ferromagnet material with an initial magnetization curve which shows the following properties of the material:
 - a. remanance of 13,000 Gauss
 - b. saturation magnetization of 14000 G
 - c. coercive field of 800 Oe
 - d. initial permeability of 5.8 G/Oe
 - e. maximum permeability of 15 G/Oe
 - f. maximum BH product of 7×10^6 G Oe
29. The magnetic moment of an electron due to its spin is called the Bohr magneton and is defined as $eh/4\pi m_e$. The number of atoms per BCC unit cell in Fe is 2 and the lattice parameter is 2.866 angstroms. Use this data and the electron configuration of Fe ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$) to calculate the magnetic moment per unit volume for Fe.

Ferromagnetic Properties

30. The net magnetic moment per atom in Ni is 0.6 Bohr magnetons ($eh/4\pi m_e$). The density of Ni is 8.9 Mg/m^3 , and the atomic weight is 58.7 g/mol. Calculate the saturation magnetization (A/m) for Ni.
31. Consider the data in the table below. Use these data to draw a hysteresis loop for this material.
 - a. What is the remanent induction, B?
 - b. What is the coercive field?
 - c. On the hysteresis loop, draw what you would expect for the initial magnetization of the material, from the demagnetized state.

$H(\text{A/m}) \times 10^4$	$B(\text{web/m}^2)$
6	0.65
1	0.58
0	0.56
-1	0.53
-2	0.46
-3	0.30

-4	0.00
-5	-0.44
-6	-0.65

Ferroelectrics

32. A piezoelectric spark igniter is made using a disk that has a 4 mm diameter and 30 mm height. Calculate the voltage generated if the g coefficient for the materials is 40×10^{-3} V-m/N. Assume a compressive force of 9000 N is applied on the circular face.
33. A hysteresis loop (polarization vs. electric field) for ferroelectric has a saturation polarization of 1×10^{-7} C/m², a remanent polarization of 7×10^{-8} C/m² and a coercive electric field of -5000 V/m. Draw this loop and then determine the voltage required to eliminate the polarization in a 0.2 cm thick dielectric made from this material.

Ferroelectrics and Superconductors

34. A hysteresis loop (polarization vs. electric field) for a ferroelectric has a saturation polarization of 1×10^{-7} C/m², a remanent polarization of 7×10^{-8} C/m² and a coercive electric field of -5000 V/m. Draw this loop and then determine the voltage required to eliminate the polarization of a 0.2 mm thick dielectric made from this material.
35. For a superconducting material at a temperature T below the critical temperature T_C , the critical field, $H_C(T)$, depends on the temperature according to the relationship

$$H_C(T) = H_C(0) \left(1 - \left(\frac{T^2}{T_C^2} \right) \right)$$

Where $H_C(0)$ is the critical field at 0 K.

Consider the data below for tin and lead and then answer the questions. Remember that $\mu_0 = 4\pi \times 10^{-7}$ H/m

- Calculate the critical magnetic field for tin at 1.5 K.
- To what temperature must lead be cooled in a magnetic field of 20,000 A/m for it to be superconducting?

Material	Critical Temperature (K)	Critical Magnetic Flux Density ($\mu_0 H_C$) (tesla)
Tin	3.72	0.0305
Lead	7.19	0.0803

Section 2. Characterization and Testing

Some Useful Information

Physical constants:

$$h = 6.63 \times 10^{-34} \text{ J s}$$

$$c = 3.00 \times 10^8 \text{ m s}^{-1}$$

$$N = 6.02 \times 10^{23} \text{ molecules mol}^{-1}$$

$$\epsilon_0 = 8.85 \times 10^{-12} \text{ C V}^{-1} \text{ m}^{-1}$$

$$\text{For protons } g_1 \mu_N = 2.82 \times 10^{-26} \text{ J T}^{-1}$$

Conversions:

$$1 \text{ W} = 1 \text{ J s}^{-1}$$

$$1 \text{ eV} = 8065.5 \text{ cm}^{-1}$$

Assorted equations (useful or not):

$$E = n^2 h^2 / 8 mL^2 = h \nu;$$

$$E = (v+1/2) h \nu_0 = (v + 1/2) (h/2\pi) (k/m)^{1/2};$$

$$E = -Z^2 \mu e^4 / 8 \epsilon_0^2 h^2 n^2;$$

$$E = h\nu = \gamma (h / 2\pi) B = g_1 m_N B;$$

$$K_{IC} = Y \sigma_f (\pi a)^{1/2}$$

$$n\lambda = 2d \sin \theta$$

$$d_{hkl} = a / (h^2 + k^2 + l^2)^{1/2}$$

For fcc diffraction occurs when h, k and, l are unmixed.

For bcc diffraction occurs when h+k+l is an even number

$$N = 2^{G-1}$$

Part 1. Multiple choice and true-false questions

1. Calculate the energy per mole of photons for radiation of wavelength 400 nm (blue).
 - a. 299 J mol⁻¹
 - b. 299 kJ mol⁻¹
 - c. 29900 J mol⁻¹
 - d. none of the above
2. Estimate the lifetime of a system that gives a spectral emission of linewidth 5 MHz.
 - a. 3 × 10⁻⁶ s
 - b. 1 s
 - c. 10⁻⁸ s
 - d. 3 × 10⁻⁸ s
 - e. 2 × 10⁻⁹ s

3. In a photoelectric cell when electrons are ejected, the number of them ejected per second is
 - a. proportional only to intensity of the light
 - b. proportional only to the frequency of the incident light
 - c. independent of both frequency and intensity of the incident light
 - d. dependent on the momentum of the incident light
4. A black body is
 - a. an ideal emitter
 - b. an ideal absorber
 - c. a material that gives off black body radiation
 - d. a body that gives off radiation at short wavelength; referred to as the ultraviolet
 - e. catastrophe
 - f. all the above
5. A photon with energy of one electron volt ($1 \text{ eV} = 1.602 \times 10^{-12} \text{ ergs}$) has a wavelength of:
 - a. $1.86 \times 10^{-3} \text{ cm}$
 - b. 3660 angstroms
 - c. $3.0 \times 10^{-5} \text{ cm}$
 - d. 12,400 angstroms
6. Which of the following is not quantized?
 - a. vibrational motion
 - b. translational motion
 - c. nuclear spin states
 - d. phonon modes
7. Neutrons used for neutron diffraction experiments are generated in a reactor and slowed to thermal energies by repeated collisions with a moderator such as
 - a. steel
 - b. lead
 - c. graphite
 - d. cobalt
 - e. none of these
8. The fundamental limitations of light optical systems limit resolution to features which are approximately _____ or larger.
 - a. 0.01 micrometers
 - b. 0.1 micrometers
 - c. 1.0 micrometers

- d. 10 micrometers
 - e. none of the above
9. The elements that cannot be analyzed by Auger electron spectroscopy are:
- a. Ba and La
 - b. Cl and Ar
 - c. H and He
 - d. none of the above
10. Changes in the binding energy of core electrons in carbon atoms can occur due to (choose all applicable)
- a. Change in chemical environment of the atom
 - b. Change in oxidation state
 - c. Change in crystal structure
 - d. none of the above
11. The relationship between absorbance and transmittance (T) is:
- a. $A = \log(1.0 / T)$
 - b. $A = 1.0 / T$
 - c. $A = \log(T)$
 - d. $A = 100.0 \log(T)$
12. The molar absorption coefficient of a solute at 600 nm is $3000 \text{ L mol}^{-1} \text{ cm}^{-1}$. If light of 600 nm wavelength passes through a 5 cm long cell with that solute in it, 88% of the light was absorbed. What is the concentration of that solution?
- a. $8.52 \times 10^{-7} \text{ mol L}^{-1}$
 - b. $4.26 \times 10^{-6} \text{ mol L}^{-1}$
 - c. $7.05 \times 10^{-4} \text{ mol L}^{-1}$
 - d. $1.41 \times 10^{-4} \text{ mol L}^{-1}$
 - e. none of the above
13. In a dispersive instrument, the resolution of the spectrum is controlled by (choose all applicable):
- a. size of the gratings
 - b. quality of the prism
 - c. width of the slits in a variable filter
 - d. distance traveled by a moving mirror
14. In an FT-IR, the resolution of the spectrum is controlled by:
- a. size of the gratings
 - b. quality of the prism
 - c. width of the slits in a variable filter

- d. distance traveled by a moving mirror
15. Stretching vibrations have, in general, a higher frequency than bending vibrations
- True
 - False
16. Which of the molecules listed does not show an absorption in the infrared?
- H₂
 - HCl
 - CO₂
 - H₂O
 - CH₃CH₃
 - CH₄
 - CH₃Cl
17. To observe an infrared spectrum upon absorption of energy:
- a change in dipole moment must occur
 - a change in polarizability must occur
 - the molecule must possess a dipole moment
 - the molecule must not possess a dipole moment
 - none of the above
18. A common source of electromagnetic radiation for infrared absorption spectroscopy is a
- hollow cathode lamp
 - Nernst glower
 - deuterium lamp
 - xenon arc lamp
19. The intensity of the Raman signals is dependent on the frequency (ν) of the incident radiation as
- ν
 - ν^2
 - ν^3
 - ν^4
 - ν^5
20. To observe a Raman spectrum upon absorption of energy,
- a change in dipole moment must occur
 - a change in polarizability must occur
 - the molecule must possess a dipole moment
 - the molecule must not possess a dipole moment

- e. none of the above
21. In nuclear magnetic resonance (NMR) spectroscopy, chemical shifts are caused primarily by
- the number of NMR-active nuclei on adjacent atoms
 - the number of identical NMR-active nuclei on a particular atom
 - polar interactions between the NMR-active nuclei and the solvent
 - magnetic shielding of the NMR-active nuclei by electrons in the molecule
22. Polyethylene is a synthetic polymer or plastic with many uses. 1.40 g of a polyethylene sample was dissolved in enough benzene to make 100.0 mL of solution, and the osmotic pressure was found to be 1.86 torr at 25°C. What is the molar mass of the polyethylene?
- $1.06 \times 10^8 \text{ g mol}^{-1}$
 - $1.19 \times 10^4 \text{ g mol}^{-1}$
 - 5270 g mol⁻¹
 - $3.39 \times 10^6 \text{ g mol}^{-1}$
 - $1.40 \times 10^5 \text{ g mol}^{-1}$
23. The turbidity of solutions is the result of:
- absorption of light at specific wavelengths
 - inelastic scattering of light at specific wavelengths
 - elastic scattering of light at specific wavelengths
24. In atomic absorption experiments, the primary light source used is
- He-Ne laser
 - Kr⁺ laser
 - Xe lamp
 - Hg lamp
 - hollow cathode lamp
25. Differential scanning calorimetry (DSC) is a technique useful in determining
- glass transition temperatures
 - softening points of amorphous polymers and glasses
 - melting point of a crystalline polymer
 - all of the above
26. Which method could not be used to determine if a glass sample contains any borosilicate?
- Auger spectroscopy
 - XPS
 - NMR
 - DSC

27. Which of the following techniques would yield the most complete information on the oxidation states of elements on surfaces?
- scanning electron microscopy
 - scanning tunneling microscopy
 - X-ray fluorescence spectroscopy
 - X-ray photoelectron spectroscopy
 - Auger spectroscopy
28. What of the following is a definition of the mechanical property referred to as hardness?
- A measure of a material's resistance to localized plastic deformation such as a small dent or scratch.
 - A measure of the plastic deformation occurring at high temperature under constant load over a long time period.
 - A measure of the force applied to induce bending in a material.
 - None of the above
29. When an electron beam strikes a specimen, several signals can be generated from the electron beam-specimen interaction. Which signal is usually used in the study of surface analysis?
- secondary Electrons
 - backscattered Electrons
 - Auger Electrons
 - characteristic X-rays
 - none of the above
30. What is the point group for IF_5 ?
- C_{3v}
 - D_{3h}
 - C_{4v}
 - D_{4h}
 - C_1
31. Calculate the energy per mole of photons for radiation of wavelength 632 nm (He-Ne-red).
- 189 J mol^{-1}
 - 189 kJ mol^{-1}
 - 18.9 J mol^{-1}
 - $2 \times 10^{-4} \text{ J mol}^{-1}$
32. In a photoelectric cell when electrons are ejected, the number of them ejected per second is
- proportional only to intensity of the light

- b. proportional only to the frequency of the incident light
 - c. independent of both frequency and intensity of the incident light
 - d. dependent on the momentum of the incident light
33. A black body is
- a. an ideal emitter
 - b. an ideal absorber
 - c. a material that gives off black body radiation
 - d. a body that gives off radiation at short wavelength; referred to as the ultraviolet
 - e. catastrophe
 - f. all the above
34. An element that cannot be analyzed by Auger electron spectroscopy is:
- a. Li
 - b. Ne
 - c. Hg
 - d. U
35. Changes in the binding energy of core electrons in carbon atoms can occur due to (choose all applicable)
- a. change in chemical environment of the atom
 - b. change in oxidation state
 - c. change in crystal structure
 - d. none of the above
36. The molar absorption coefficient of a solute at 600 nm is $1000 \text{ L mol}^{-1} \text{ cm}^{-1}$. If light of 600 nm wavelength passes through a 10 cm long cell with that solute in it, 50% of the light is transmitted. What is the concentration of that solution?
- a. $1.0 \times 10^{-1} \text{ mol L}^{-1}$
 - b. $1.0 \times 10^{-2} \text{ mol L}^{-1}$
 - c. $2.0 \times 10^{-1} \text{ mol L}^{-1}$
 - d. $4.0 \times 10^{-1} \text{ mol L}^{-1}$
37. The rate of corrosion of a spinning metal propeller is increased by the work hardening of the part and its local rotation rate
- a. true
 - b. false
38. Which method would be best to determine if a glass sample contains any lead?
- a. Auger spectroscopy
 - b. XPS
 - c. XRD

- d. XRF
39. The Vickers hardness is most representative of what quantity
- toughness
 - yield strength
 - tensile strength
 - none of the above
40. For the calculation of engineering stress versus strain the cross section area of the sample
- is assumed to be constant and equal to the initial value.
 - is assume to continuously vary during the course of the test.
 - is assumed to be constant and equal to the value at the end of the test.
 - is assumed to be constant and equal to the value at the yield strength.
41. The velocity of sound in a metal is:
- independent of its density
 - dependent on the oxidation state of the material
 - dependent on the density
 - proportional to the ductility
42. The T , T_d , T_h , O and O_h Schoenflies notation are representative of what crystal system?
- Hexagonal
 - Cubic
 - Tetragonal
 - Monoclinic
 - Triclinic

Part 2. Short Answer

- Show schematically, using an energy level diagram, the process that produces continuum X-rays, characteristic X-rays, and Auger electrons.
- The characteristic emission from K atoms when heated is purple and lies at 770 nm. On close inspection, the line is found to have two closely spaced components, one at 766.70 nm and the other at 770.11 nm. Account for this observation.
- Describe a high-resolution NMR spectrum of toluene, $C_6H_5CH_3$. Identify all multiplets.
- Describe how etching reveals features on a single-phase metallographic sample; use a drawing to highlight your points.
- Discuss how one might obtain quantitative information concerning the diffusion coefficient of C in Fe by using carburization treatments of Fe combined with conventional metallography.
- Consider using lead as a creep sample. Over what temperature range would you expect creep to occur?

- Graph a stress versus strain curve for a material with the following parameters; $E = 70$ GPa, Y.S. = 410 MPa, T.S. = 520 MPa, % elongation at failure = 12%. Be sure to include the units of your variables.
- Discuss the effect of interior flaws, i.e., voids, on the tensile strength.
- Show schematically the process that produces continuum X-rays, characteristic X-rays, and Auger electrons.
- The following absorption data are obtained for solutions of oxyhemoglobin in pH 7 buffer at 575 nm in a 1 cm cell. The molar mass of hemoglobin is 64.0 kg/mol.

Concentration / g cm^{-3}	% Transmission
3×10^{-4}	53.5
5×10^{-4}	35.1
10×10^{-4}	12.3

- Is Beer's law obeyed?
 - What is the molar absorption coefficient?
- Calculate the ratio of the number of proton spins in the lower state to the number in the higher state for a 1000MHz NMR at room temperature.
 - Describe a high-resolution NMR spectrum of ethanol, $\text{CH}_3\text{CH}_2\text{OH}$. Identify all multiplets.
 - Describe how etching reveals features on a metallographic sample.
 - What is the advantage of using an oil immersion lens in light microscopy and what is the cause of this benefit?
 - Discuss how one might obtain quantitative information concerning the diffusion coefficient of C in Fe by using carburization treatments of Fe combined with conventional metallography.
 - On the same axes, sketch the typical stress-strain curves for the following: (a) ductile metal, (b) ceramic in tension, (c) polymer. Briefly discuss the appearance and shape of the curves based on strength, ductility and toughness.
 - How does fatigue testing differs from tensile testing?

Part 3. Calculations

- An ESCA (XPS) electron was found to have a kinetic energy of 1073.5 eV when ejected with an Mg $K\alpha$ source ($\lambda = 0.98900$ nm) and measured in a spectrometer with a work function of 14.7 eV. What is the binding energy for the emitted electron?
- The fundamental vibrational frequency of H^{35}Cl is $8.967 \times 10^5 \text{ s}^{-1}$. What would be the separation (in nm) between the vibrational lines of H^{35}Cl and H^{37}Cl , if the force constants are assumed to be the same? (Masses: H 1.008 amu; ^{35}Cl 34.969 amu; ^{37}Cl 36.965 amu).
- Compound A has a molecular weight of 98.4 and a heat of fusion of 1.63 kcal/mole. Compound B has a molecular weight of 64.3 and melts at approximately the same temperature as compound A. Samples of 500 mg of each yield differential thermal analysis (DTA) peak areas of 60.0 and 45.0 cm^2 for A and B, respectively. What is the heat of fusion of compound B?
- A high-strength steel has a yield strength of 1460 MPa and a K_{IC} of 98 $\text{MPa m}^{1/2}$. Calculate the size of a surface crack that will lead to catastrophic failure at an applied stress of $1/2$ Y.S.

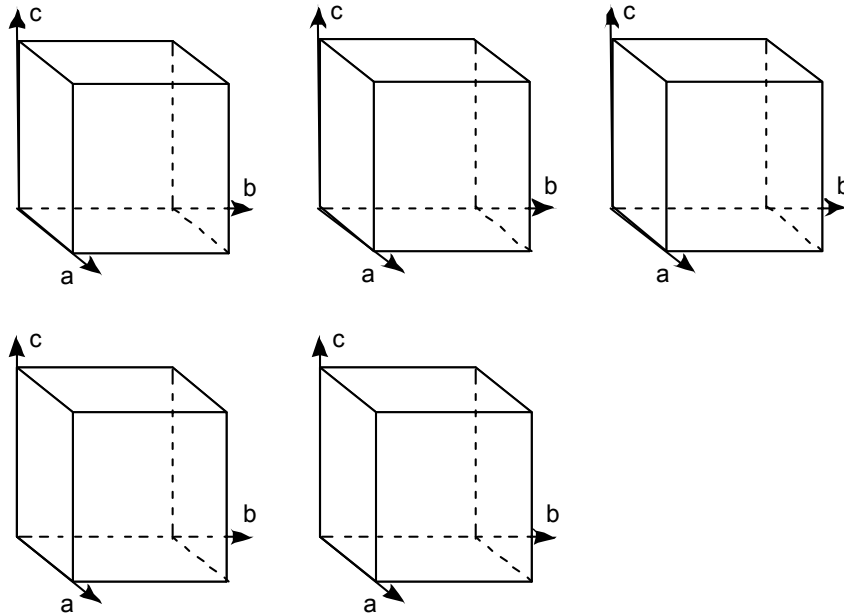
- Sketch the expected x-ray diffraction pattern, for the first four $n=1$ peaks for Ni an fcc metal ($r = 0.125$ nm) using $\lambda = 0.1542$ nm.
- Would you expect more or less separation between the peaks if a shorter wavelength of radiation was used? Explain your answer.
- Sketch the idealized mass spectra of $^{12}\text{C}_6^{1}\text{H}_5^{16}\text{O}^1\text{H}$, and $^{12}\text{C}_6^{1}\text{H}_5^{14}\text{N}^1\text{H}_2$. Can you identify which compound is which from the mass spectra?

Useful formula for a molecule of the form $\text{C}_w\text{H}_x\text{O}_z\text{N}_y$:

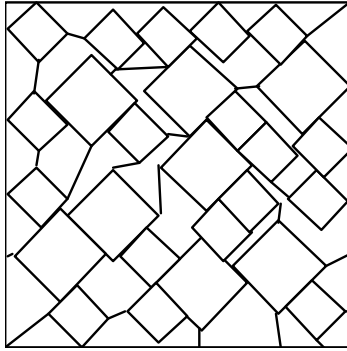
$$100[(P_{M+1})/P_M] = 0.015x + 1.11w + 0.37y + 0.037z$$

$$100[(P_{M+2})/P_M] = 0.20z + 0.006w(w-1) + 0.004wy + 0.0002wx$$

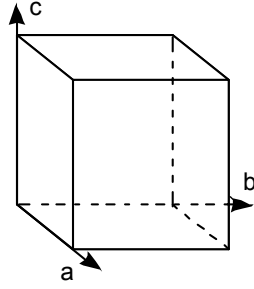
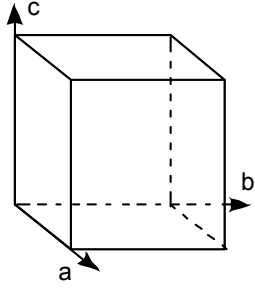
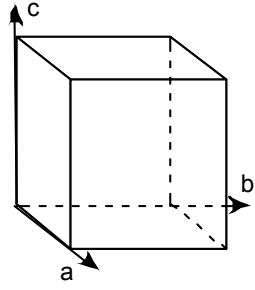
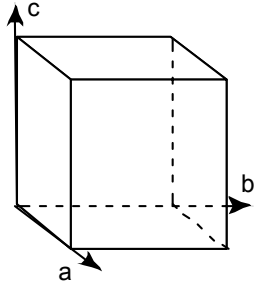
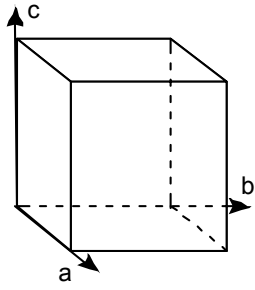
- A metal naphthenate sample, ashed and diluted to a fixed volume, gave a scale reading of 29. Two additional solutions prepared in the same way (with the same unknown) plus 25 and 50 ppm of barium, respectively, gave readings of 53 and 78. How much barium was in the original sample?
- In the unit cell figures below sketch the planes for the first five planes on which x-ray diffraction would occur in a bcc crystal structure. Indicate the position of the relevant atoms within those planes.



- Calculate the Grain Size Number for the following $2'' \times 2''$ picture if it was taken at magnifications of 50X, 100X, and 250X.



11. Consider a 1.000 cm thick steel plate that has been joined by a weld; you may assume that the welded area has been machined so that it is perfectly parallel with the plate surfaces. If you can detect a 1% change in the intensity; calculate the size of a flaw, such as a void, that could be detected. ($\mu = 0.293 \text{ mm}^{-1}$).
12. Draw a schematic diagram of the output for the ultrasonic inspection of the same steel part. You may assume that the void is anywhere in the weld except for at the surface. Do not assume that the void cross-sectional area is so small that it cannot be detected. Assume that there is 2.0 cm of water between the transducer and the steel part. $V_{\text{H}_2\text{O}} = 1,483 \text{ m/s}$, $V_{\text{SS}} = 5760 \text{ m/s}$, $\rho_{\text{H}_2\text{O}} = 1 \text{ gm/cm}^3$ and, $\rho_{\text{SS}} = 7.16 \text{ g/cm}^3$.
13. The addition of carbon or boron to bcc iron ($r = 0.124 \text{ nm}$) produces considerable strain in the overall lattice. For carbon this strain or overall change in the lattice parameter, a , is about 2%. Calculate the x-ray diffraction pattern for pure iron and for steel (iron-carbon) for the first four $n=1$ using $\lambda = 0.1542 \text{ nm}$. Comment on the resolution need to discriminate between pure iron and steel.
14. Would you expect more or less separation between the peaks if a longer wavelength of radiation was used? Explain your answer.
15. An unknown sample was diluted to a fixed volume, and gave an arbitrary unit scale reading of 29. Two additional solutions prepared in the same way (with the same unknown) plus 25, 50 and, 75 ppm of barium, respectively, gave readings of 53 and 78 and 98. How much barium was in the original sample?
16. In the unit cell figures below sketch the planes for the first five planes on which x-ray diffraction would occur in an fcc crystal structure. Indicate the position of the relevant atoms within those planes.



Section 3. Thermodynamics and Processing

Some Useful Information

Physical Constants and Symbols:

1 atm = 1 atmosphere = 101,325 Pa = 101.3 kPa = 1 bar = 760 torr = 760 mm Hg

1 cal = 1 gram-calorie = 4.18 J

1 L = 1 liter = 1 dm³

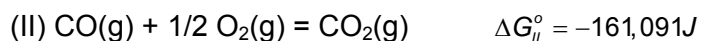
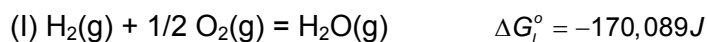
<u>Quantity</u>	<u>Symbol</u>	<u>Value</u>
internal energy	U	
enthalpy	H	
entropy	S	
Gibbs free energy	G	
Helmholtz free energy	A	
speed of light in vacuum	c	$2.9979 \times 10^8 \text{ m s}^{-1}$
Planck's constant	h	$6.6261 \times 10^{-34} \text{ J s}$
electron charge	e	$1.6022 \times 10^{-19} \text{ C}$
electron mass	m_e	$9.1094 \times 10^{-31} \text{ kg}$
proton mass	M_n	$1.6726 \times 10^{-27} \text{ kg}$
atomic mass unit	U	$1.6606 \times 10^{-24} \text{ g}$
Rydberg constant	R	$1.09737 \times 10^5 \text{ cm}^{-1}$
Avogadro's number	N_0	$6.02221 \times 10^{23} \text{ molecules}$
Faraday constant	F	$96458.3 \text{ C mol}^{-1}$
ideal gas constant	R	$8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$ $1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$ $0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1}$ $0.082058 \text{ L atm K}^{-1} \text{ mol}^{-1}$
Boltzmann constant	k_B	$1.3807 \times 10^{-23} \text{ J K}^{-1}$

Periodic Table of the Elements

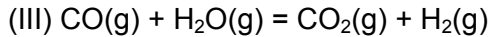
1 H 1.01																	2 He 4.00
3 Li 6.94	4 Be 9.01											5 B 10.8	6 C 12.0	7 N 14.0	8 O 16.0	9 F 19.0	10 Ne 20.2
11 Na 23.0	12 Mg 24.3											13 Al 27.0	14 Si 28.1	15 P 31.0	16 S 32.1	17 Cl 35.5	18 Ar 40.0
19 K 39.1	20 Ca 40.1	21 Sc 45.0	22 Ti 47.9	23 V 50.9	24 Cr 52.0	25 Mn 54.9	26 Fe 55.8	27 Co 58.9	28 Ni 58.7	29 Cu 63.5	30 Zn 65.4	31 Ga 69.7	32 Ge 72.6	33 As 74.9	34 Se 79.0	35 Br 79.9	36 Kr 83.8
37 Rb 85.6	38 Sr 87.6	39 Y 88.9	40 Zr 91.2	41 Nb 92.9	42 Mo 95.9	43 Tc 98.9	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 *La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po 209.0	85 At 210.0	86 Rn (222)
87 Fr (223)	88 Ra 226.0	89 ‡Ac 227.0	104 Unq 261.1	105 Unp 262.1	106 Unh 263.1	107 Uns 262.1	108 Uno (265)	109 Une (266)									
			*58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm 144.9	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0	
			‡90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu 237.0	95 Am 243.1	96 Cm 247.1	97 Bk 247.1	98 Cf 242.1	99 Es 252.1	100 Fm 257.1	101 Md 258.1	102 No 259.1	103 Lr 260.1	

Part I – Short Problems

1. Compute the pressure of a gas mixture containing 20 g N₂ and 50 g Ar in 1.00 m³ of volume at 300.00 K. Molecular Weight of N₂ is 28 and Ar is 40, R = 8.3146 J/mol K
2. Calculate ΔU, when one mole of Argon gas is heated at constant volume from 25°C and 1 bar.
3. Compute the entropy of mixing of one mole of liquid ³He with 10 moles of ⁴He at 5 K assuming that the solution is ideal, i.e., similar to an ideal gas mixture.
4. The standard Gibbs energy changes at 1400 K for the combustion of H₂ and CO are as follows:



Calculate the equilibrium constant at 1400 K for the reaction



5. A system is composed of a solid phase CaCO_3 , solid phase CaO , and a gas phase consisting of CO_2 . The following equilibrium occurs:



How many components are there? What are the degrees of freedom?

6. The values of silver gas pressure over liquid Ag-Au alloys at 1350 K are as follows:

$P_{\text{Ag}} \text{ (Pa):}$	3.140	2.393	1.583	1.212	0.882	0.361
$X_{\text{Au}}:$	0.0	0.20	0.40	0.50	0.60	0.80

Calculate a_{Ag} at $X_{\text{Ag}} = 0.5$.

7. The standard Gibbs energy of formation of $\text{Hg}_2\text{Cl}_2\text{(s)}$ is $-210,330 \text{ J mol}^{-1}$ at 25°C . Construct a cell in which $2\text{Hg (l)} + \text{Cl}_2 \text{(g)} = \text{Hg}_2\text{Cl}_2\text{(s)}$ takes place and compute the emf of the cell.

8. The Clausius equation for a ferromagnet is

$$dU = T dS + H dM$$

where U = Internal energy, S = entropy, H = magnetic field, T = absolute temperature, M = magnetic dipole moment per unit volume. The Gibbs energy is

$$G = U - TS - HM$$

What is the correct expression for dG ?

9. Consider the face centered cubic crystal structure and the planes (100), (110), and (111). On the basis of the degree of close packing associated with each plane, rank these planes in order of their growth velocity during freezing.
10. The dendrite arm spacing (DAS) is dependent on the cooling rate, k , by an equation of the form $\text{DAS} = A k^{-n}$, where A and n are constants. Suppose for M-X alloy, DAS was measured as 100 and $10\mu\text{m}$ at the cooling rates 0.1 and 60 K/s respectively. Determine A and n for the alloy.
11. A Carnot heat engine operates between reservoirs at 1200°C and 200°C . Assuming that the working substance is a kilomole of ideal gas, calculate the efficiency of the heat engine.
12. The temperature dependence of the sublimation pressure of solid Cl_2 is summarized in the following table:

$T(^{\circ}\text{C})$	-112	-126.5
$P(\text{atm})$	0.00352	0.00035

Compute the heat of sublimation.

13. For a ferromagnetic substance with magnetization, M , in an applied magnetic field, H , the Helmholtz energy, A , satisfies:

$$dA = -S dT + M dh$$

where T is the absolute temperature and S is the entropy. The thermal coefficient of magnetization is $(\partial M / \partial T)_H$. Use the Maxwell relations to show that $(\partial M / \partial h)_T$ equals:

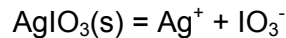
- (a) $(\partial^2 A / \partial T^2)_H$ (b) $-(\partial S / \partial H)_T$
 (c) $-(\partial S / \partial T)_H$ (d) $-(\partial M / \partial S)_T$

14. A and B are soluble in the liquid phase. At a point in the phase diagram where solid A, solid B, and their liquid solution coexist, how many independent thermodynamic variables are required to describe the equilibrium?

Hint: Gibbs phase rule: $f = c - p + 2$

15. An electrochemical cell involves a one-electron transfer. Compute the equilibrium constant, K , at 298 K if $E^\circ = -0.250$ V.

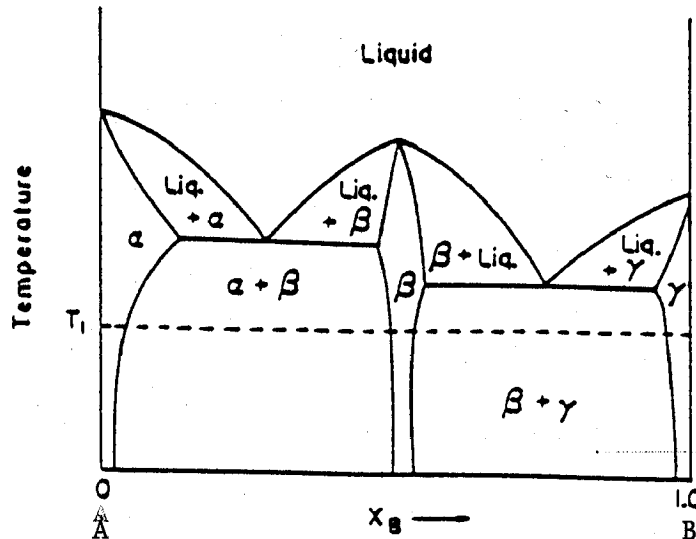
16. Calculate the equilibrium constant K_i and ΔG° for the reaction



The solubility of $\text{AgIO}_3(\text{s})$ in water at 25°C is 1.42×10^{-4} moles. Assume that the Debye-Huckel limiting equation, $(\ln \gamma_{\pm}) = (Z_+ Z_-) 1.171 l^{0.5}$ is valid.

17. For the binary A – B system draws the following for temperature T_1 :

- Gibbs energy vs. composition curves for α , β , and γ phases
- Activities of components A and B at $T = T_1$; pure solids A and B are the standard states.



18. A new phase is forming within a solid. At time t , the fraction, α , of the total volume of the solid occupied by the new phase is given by the Avrami equation:

$$\alpha = 1 - \exp(-kt^n)$$

Obtain a formula for the first half-life of this phase transformation in terms of the rate constant, k , and the index, n .

19. In a laboratory experiment on sintering of Al_2O_3 , at 1400°C , values of diffusion coefficient of Al_2O_3 were obtained as:

$$D = 3 \times 10^{-4} \text{ cm}^2/\text{sec}; D_0 = 40 \times 10^{-2} \text{ cm}^2/\text{sec}$$

Calculate the activation energy Q of the Al_2O_3 sintering.

Data:

$$D = D_0 e^{-(Q/RT)}; R = 8.314 \text{ J/g mole.deg}$$

20. The gas-phase irreversible reaction $2A \rightarrow B$ occurs in reactor where temperature and volume are held constant, but pressure varies. During the course of the reaction the pressure changes from its initial value of 1.0 atm (where only species A is present) to 0.75 atm. What is the fractional conversion of A?

Part II – Long Problems

1. Calculate the adiabatic flame temperature for CO burned completely with the theoretically sufficient amount of air by using the following data:

$$\Delta H^\circ_{298} (\text{combustion}) = -282,995 \text{ J mol}^{-1} \text{ of CO,}$$

$$C_p^\circ (\text{CO}_2) = 44.225 + 0.00878 T \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\text{and } C_p^\circ (\text{N}_2) = 28.58 + 0.00376 T \text{ J mol}^{-1} \text{ K}^{-1}$$

Assume that the air contains 20 % O₂ and 80 % N₂.

2. The vapor pressure of liquid zinc is given by the expression below:

$$\ln P (\text{bar}) = - (15375 / T) - 1.274 \ln T + 22.055$$

Calculate the enthalpy of vaporization at 1000 K.

3. For the reaction $\text{C(s)} + 0.5 \text{ O}_2 (\text{g}) = \text{CO (g)}$, the standard Gibbs energy change, ΔG° , is given by

$$\Delta G^\circ = -111710 - 87.66 T \text{ J}$$

Find a) the entropy change, ΔS° , and b) the enthalpy change, ΔH° , for the reaction.

4. Construct the phase diagram for graphite – diamond system from the equation

$$P (\text{atm}) = 7,007 + 26.65 T \text{ for the temperature range of 0 to 2000 K. The portion of the diagram from 0 to 600 K should be schematic.}$$

5. From the sintering data on ZnS, diffusion coefficients were measured. At 363°C, a diffusion coefficient of $3 \times 10^{-4} \text{ cm}^2/\text{sec}$ was measured; at 450°C, $1.0 \times 10^{-4} \text{ cm}^2/\text{sec}$. Determine the activation energy and diffusion coefficient constant.

6. Polysilicon deposits at a rate of $30 \times 10^{-8} \text{ cm /min}$ at 723 K. What deposition rate can be expected at 873 K if the activation energy for film deposition is 1.65 eV?

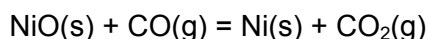
7. For solid silver, the molar heat capacity at constant pressure is:

$$C_{o P} = 21.3 + (8.535 \times 10^{-3} T) + (1.506 \times 10^{-5} T^2) \text{ J/g atom K}$$

Find the quantity of heat required to raise the temperature of 1 g atom of silver from 25°C to 900°C.

8. One mole of argon at 1 bar and T_1 and 3 moles of helium at 3 bars and at the same temperature are first mixed and then compressed isothermally to 4 bars then heated to $T_2 = 2T_1$ at constant pressure. What is the entropy change for each step and for the entire process?

9. The following equilibrium data have been determined for the reaction,



Temperature (°C)	716	793
K x 10 ⁻³	3.323	2.037

Determine ΔG_0 at 1000 K.

10. The phases ice and water coexist at the normal melting point 273.15 K (at 1 bar). At the triple point, the phases ice, and gas (steam) coexist. The vapor pressure of gas in equilibrium with the ice and water phases is 4.58 Torr (0.0061 bars). Find the temperature of the triple point.

Given: $\Delta V_{S-L} = -1.6314 \text{ cm}^3/\text{mol}$; $\Delta H^\circ_{S-L} = 6008 \text{ J/mol}$

11. The activity coefficient of aluminum in liquid Fe-Al alloys at 1600°C is determined from measurements of the equilibrium distribution of aluminum between liquid iron and liquid silver. The results over the range $0 < X_{Al} < 0.25$ can be expressed in the following concise form:

$$\ln \gamma_{Al} = 2.60 X_{Al} - 1.51$$

Find the activity of iron in a Fe-Al alloy containing 80 mol% Fe; the temperature is 1600°C.

12. Creep of a solid material is related to the viscosity. Frequently, the viscosity follows an Arrhenius behavior because movement rate depends on the activation energy for motions of imperfections. If the viscosity is $3.16 \times 10^8 \text{ Pa s}$ at 915 °C, and $3.65 \times 10^{10} \text{ Pa s}$ at 788 °C, what is this activation energy?