Department of Chemistry
Cumulative Examinations
March 5, 2005

You may choose to answer any exam from any area covered in the examination booklet. Each exam may contain multiple parts. You may answer more than one exam but each exam is scored separately and is treated as an individual examination result. Thus, answering parts of two exams with a score of 50% *would not* yield a 100% grade for this cumulative exam. Instead you would receive 50% on each examination attempted.

This booklet contains ***five*** examinations.

On your examination booklet:

1) Print your student ID number.
2) Print this Exam Booklet number: ____________
3) Print the question number you are answering.
4) Print the Exam Date.

Do not write your name anywhere on the examination booklet. Each exam will be scored anonymously. If you attempt more than one exam, *you must use a separate examination booklet for each examination*.

When you complete the examination, return the examination and your answer booklet to the proctor. Exam results will be posted on bulletin board #2B on the north side of the hall near BRWN 2124.

PURDUE
UNIVERSITY

Analytical Cumulative Examination
March 5, 2005

QUESTION 1
EACH part is worth 2 points. Give approximate answers to the following questions.
IT IS ESSENTIAL TO GIVE UNITS

What is the value of

1) the Boltzmann constant
2) kT at room temperature
3) the number of molecules (of typical size, not macromolecules) that occupy 1 cm^2 of a surface under ordinary conditions
4) the number of molecules that occupy a liter of gas under ordinary conditions
5) pKa of acetic acid
6) the proton affinity of ammonia
7) the electron affinity of dioxygen
8) the oxidation potential of water
9) the fundamental wavelength of the Nd YAG laser
10) the rate constant of an ion/molecule reaction that occurs on every collision
11) the refractive index of glass
12) the bond energy of a C-C bond
13) the bond energy of a typical hydrogen bond
14) the mass of a typical small protein
15) the velocity of a nitrogen molecule at STP
16) the dipole moment of chloroform
17) the pressure at which air exhibits maximum conductivity
18) the number of theoretical plates in a typical lc capillary column
19) the field strength of a typical "high field" magnet (NOT in MHz)
20) the position of the OH stretch in anhydrous ethanol
21) the absorption wavelength for the electronic transition in a saturated ketone
22) the mass of the characteristic neutral fragment of an aromatic nitrocompound
23) the penetration depth of a photon undergoing total internal reflection
24) the energy of visible light photons
24) the resolution in confocal microscopy
25) the dependence of Raman intensity on excitation wavelength
26) the sampling depth in XPS (ESCA)
25) the mass measurement accuracy of time of flight mass spectrometry
26) the mass of the electron
27) the detection limit for fluorescence spectroscopy in a favorable case
28) the difference in chemical shifts between methyl and methylene groups
28) the diffusion constant of a small hydrophilic compound in water
29) the quantity varied in the Michelson interferometer to measure wavelength
30) the quantity varied in a grating to measure wavelength

QUESTION 2
EACH part is worth 4 points; define all units and be as EXPLICIT as possible

a) Write the names of the four common DNA bases
b) Name and write the structures of any three of the natural amino acids
c) Draw the mechanism of the McLafferty rearrangement
d) Give the equation for any type of mass spectrometer
e) Give the fundamental equation for nmr
f) Give Beer's law

f) Give the structure of any neurotransmitter
g) Draw the structure of a self-assembled monolayer
h) Name and describe any proteolytic enzyme
i) Write the Nernst equation
j) Write the van Deempter equation

1. The lactose operon of *E. coli* is often used as an example of a mechanism regulating the expression of prokaryotic genes. Concisely describe the Lac system in the control of gene expression, using 5-bromo-4-chloro-3-indolyl-beta-d-galactoside (X-gal) and isopropyl-beta-D-thiogalactoside (IPTG).
2. Concisely describe how the Lac system can be used for detection and isolation of cloned DNA fragments.
3. Concisely provide the function of the following molecules in transcription of eukaryotic genes:

TFIIA, TFIIB, TFIID, TFIIE, TFIIF, and TFIIH

TBP

TBP associated factors (TAFs)

SP1

Glucocorticoid receptor

Histone acetylases

4. The eukaryotic transcription factors that bind DNA are often classified according to the structure of their DNA binding domains.

Provides 3 examples for known DNA binding domains, and name a transcription factor that contains a given domain.

5. Describe the mechanism through which several proteins can be produced from transcription of a human gene that contains four exons.
6. Concisely provide the function of the following molecules in prokaryotic cells:

Ribosomes

IF-1, IF-2, and IF-3

EF-Tu and EF-Ts

Argenyl tRNA synthetase

EF-G

RF-1, RF2, and RF-3

$tRNA_f^{Met}$

$tRNA^{Ala}$

16S rRNA

Inorganic Chemistry Cumulative Exam
Purdue University
March 5, 2005
Topic: Bioinorganic Chemistry

Question 1: (25 points)

According to some recent findings, all of the transition metal ions inside of cells are bound to various biomolecules. The concentration of freely available metal ions is approximately zero. After cellular synthesis of an apoenzyme (i.e., a metalloenzyme that does not yet have a metal), this new enzyme must pick up a metal ion. Explain the process by which metalloproteins obtain the requisite metal ion or ions. Hint: Metalloproteins often contain one, specific ion and not other similar ions.

Question 2: (25 points)

The enzyme superoxide dismutase (SOD) catalyzes the following reaction:

$$2\ O_2^- + 2\ H^+ \rightarrow O_2 + H_2O_2$$

This catalyzed reaction proceeds with a very fast rate constant of $k = 2 \times 10^9\ M^{-1}s^{-1}$. This rate constant shows that the enzyme functions near the diffusion limit, a very fast reaction indeed. Explain the design feature or features of this enzyme system that allow it to have the reaction proceed so rapidly.

Question 3: (25 points)

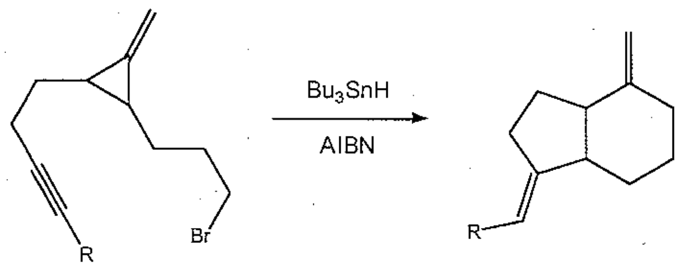
The ferredoxin class of electron transfer proteins contain a tetranuclear iron-sulfur cluster, $[Fe_4S_4(S\text{-cys})_4]^{2-/3-}$. These clusters cycle between the 3- and 2- states, as noted in the formula. Typical reduction potentials for these ferredoxin clusters are in the range of between -0.65 ⇔ -0.28 volts. The high potential iron proteins (HiPIP's) also have tetranuclear iron-sulfur clusters, $[Fe_4S_4(S\text{-cys})_4]^{1-/2-}$, but these clusters cycle between 2- and 1- states, as noted, and the typical reduction potentials are between +0.28 ⇔ +0.36 volts. Explain why these two protein systems can both have tetranuclear iron-sulfur clusters, but the reduction potentials and redox cycles are so different. Keep in mind the different redox cycles for each system (i.e., 3-/2- versus 2-/1-).

Question 4: (25 points)

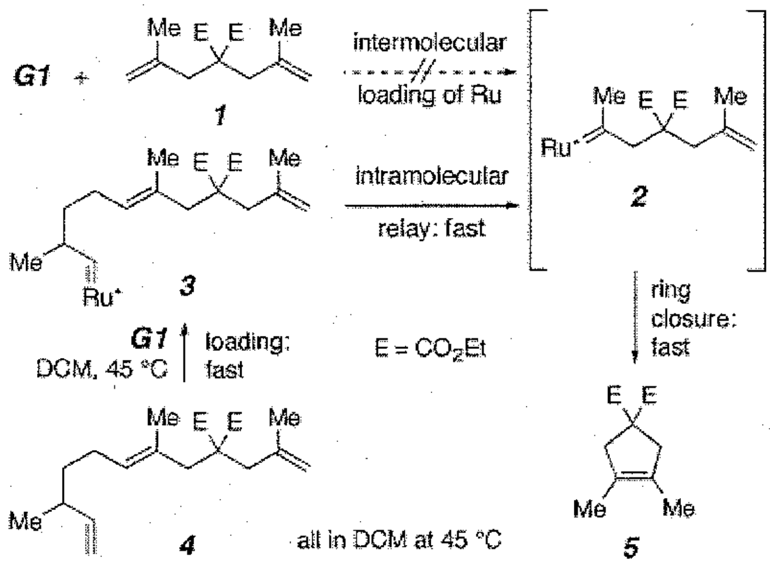
We humans transport oxygen through our blood by using the protein hemoglobin. Marine invertebrates such as clams use hemerythrin. Spiders and lobsters use hemocyanin. Each of these three proteins has a metal center or centers for reversible O_2 binding. Provide a drawing of the metal site of each system with and without O_2 bound. Your schemes need not be exactly correct, but should show the general differences between hemoglobin, hemerythrin, and hemocyanin.

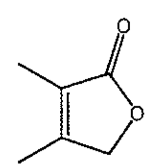
Organic Chemistry Cumulative Exam
March 5, 2005

1. (25 pts) Write a plausible reaction mechanism for the following transformation:



2. (25 pts) Ring-closing metathesis is a powerful method for the construction of carbocycles, however, it can fail when the intended substrate alkenes are sterically hindered or electronically deactivated. Hoye and coworkers have recently described a method called relay ring-closing metathesis that can obviate this problem (*J. Am. Chem. Soc.* **2004** *126*, 10210). The concept is shown below, where ***G1*** = $[(Cy_3P)_2(Cl_2)Ru{=}CHPh$. How could you use this strategy to synthesize Compound **6**?

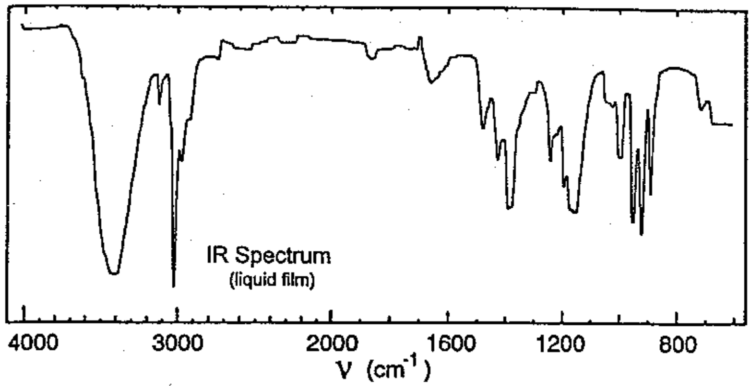


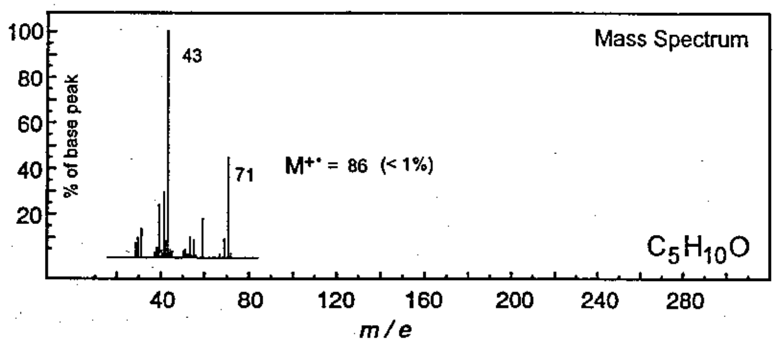


6

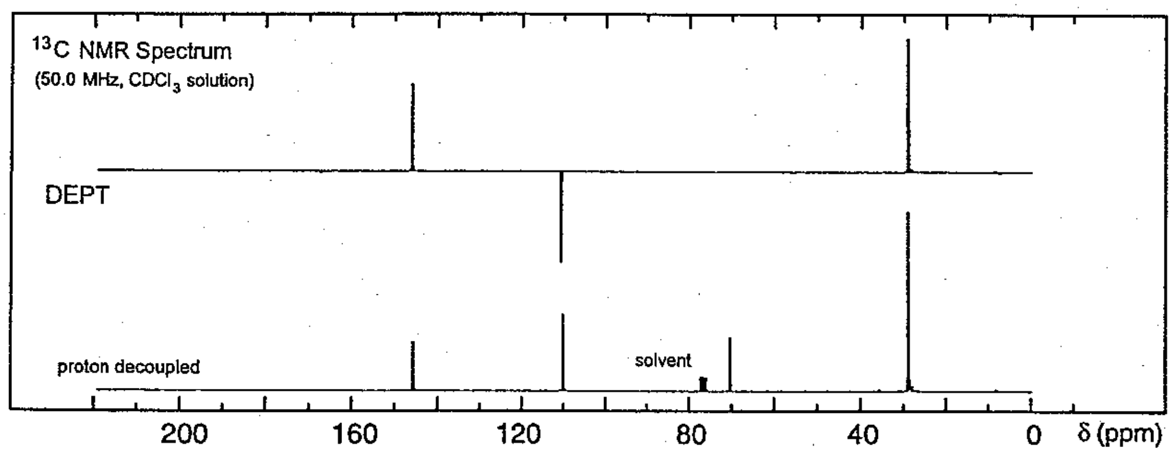
3. (25 pts each) Propose structures for the compounds that would produce the spectral data shown below.

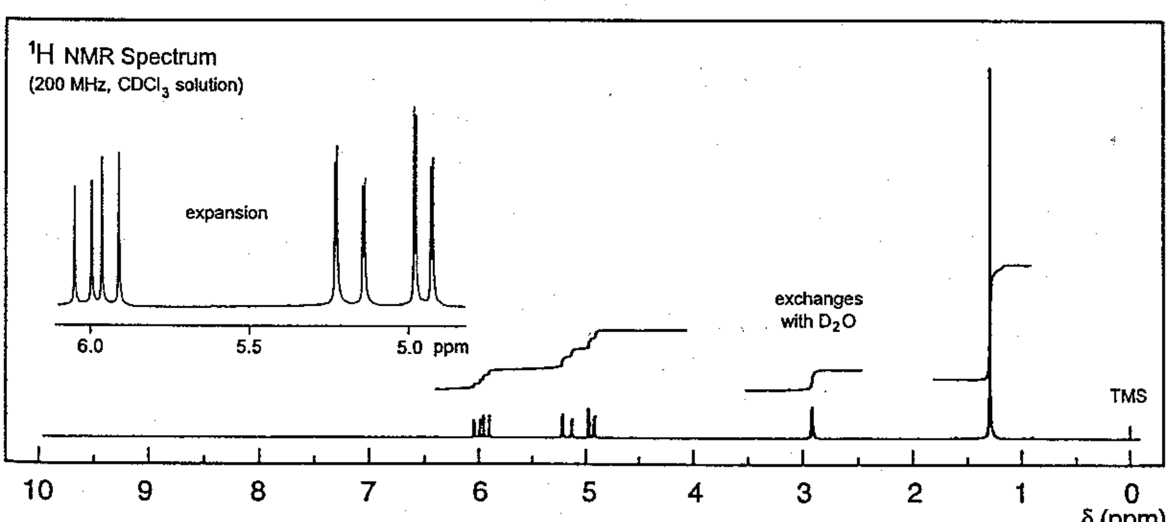
a.



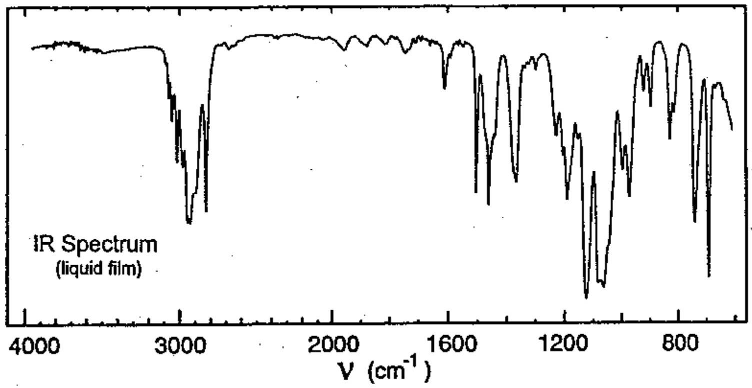


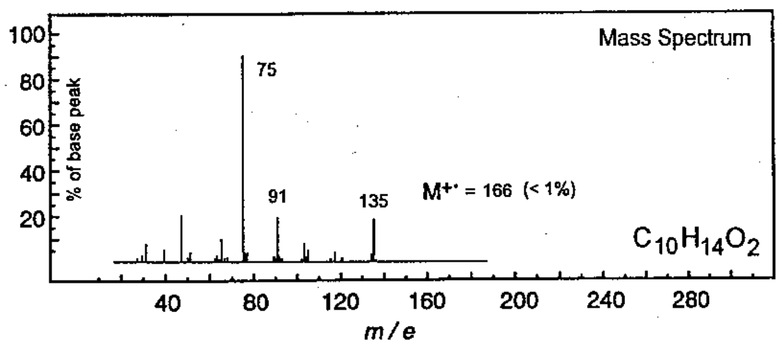
No significant UV absorption above 220 nm





3.b.

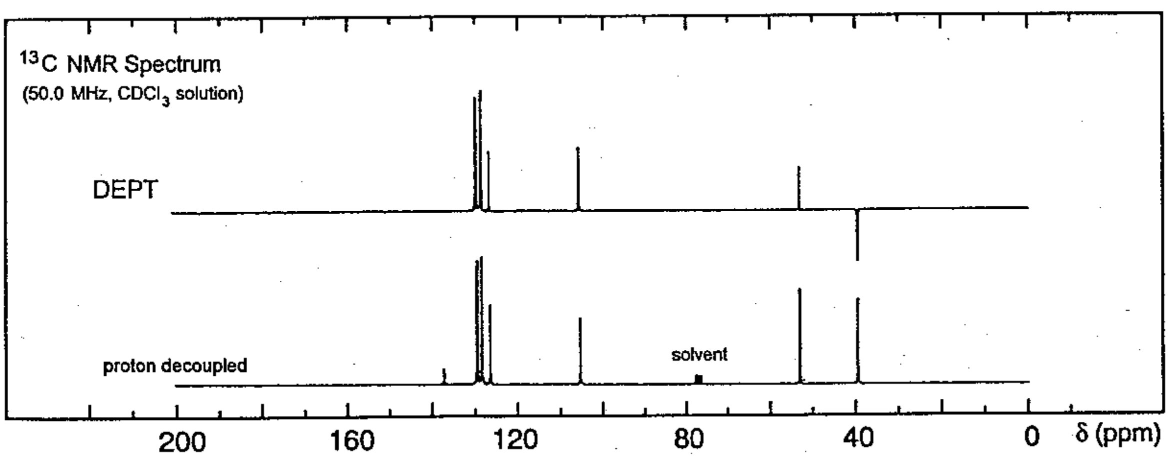


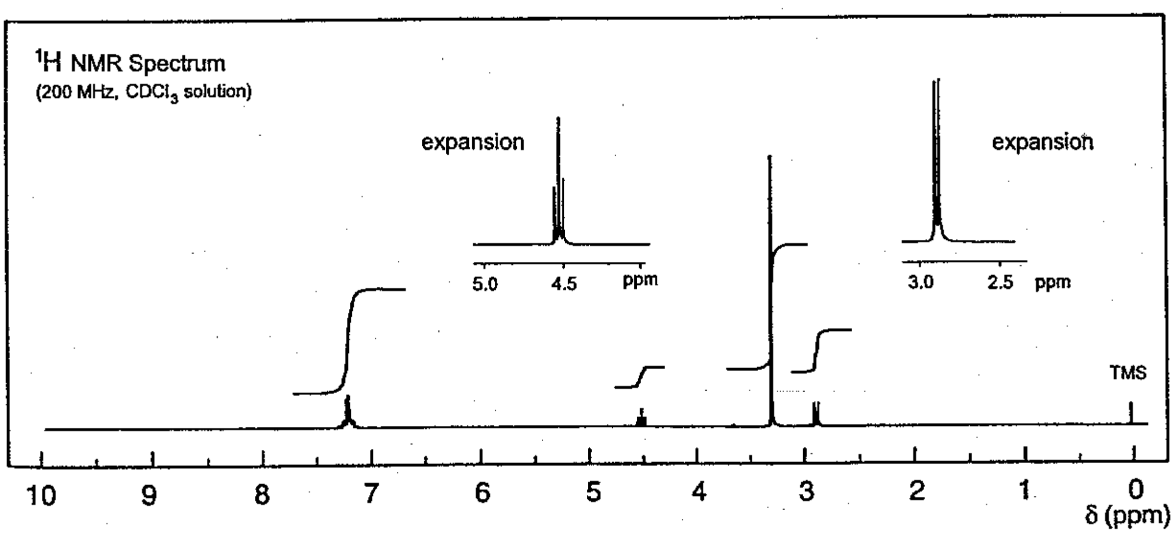


UV Spectrum

λ_{max} 262 nm ($\log_{10}\varepsilon$ 2.3)

solvent : methanol





(1) Surface active molecules have the tendency to accumulate at the air-water interface to form a monolayer. The Gibbs free energy for such a system is

$$G = G^{water} + G^{air} + G^{mono} + \gamma A \qquad (1)$$

γ.....interfacial tension
A....unit area
G^{water}, G^{air}, G^{mono}....Gibbs free energy of the water, air, and monolayer phases

(a) What is the physical meaning of the term "γA"?

(b) Show that

$$dG^{mono} = -S^{mono}dT + \gamma dA + \sum_i \mu_i dn_i^{mono}{}_i \qquad (2)$$

μ_i....chemical potential of component i
n_i.....amount of molecules of type i

(c) Derive the Gibbs surface tension equation that provides a relationship between surface tension γ and chemical potential μ (hint: dT=0)

$$d\gamma = -\sum_i \Gamma_i d\mu_i \qquad (3)$$

with $\Gamma_i = \frac{n_i}{A}$

(d) Show that

$$\Gamma^{mono} = -RTc\left(\frac{\partial \gamma}{\partial c}\right)_T \qquad (4)$$

if $\Gamma^{air}=\Gamma^{water}=0$.

c....concentration of surfactant molecules

(e) Describe in your own words why surface active molecules like surfactants and phospholipids accumulate at the air-water interface!

(2) The motion of solutes is well described by Fick's laws of diffusion which are (for the one dimensional case)

$$\text{Fick's first law: } J = -D\frac{dc}{dx} \tag{5}$$

$$\text{Fick's second law: } \frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \tag{6}$$

The thermodynamic driving force F_d and the frictional force F_f for the molecular motion are then given by

$$F_d = -\frac{RT}{c}\left(\frac{dc}{dx}\right) \tag{7}$$

$$F_f = fv \tag{8}$$

f....frictional coefficient
v....velocity
D...diffusion coefficient

(a) What is the physical meaning of equations (5) and (6)!

(b) Show that D and f are related via the Einstein equation

$$D = \frac{kT}{f} \tag{9}.$$

f.....frictional coefficient
v....velocity

c) Confocal fluorescence correlation spectroscopy is a modern imaging technique that relies on the measurement of average diffusion times of fluorescent probes during their movement through the confocal spot (confocal spot size corresponds to size of *Ecoli* bacterium). On the basis of equation 9, several fascinating experiments are possible, such as the study of receptor-ligand interactions in cellular systems or the observation of the aggregation behavior of photoluminescent semiconductor nanoparticles in blood serum to explore their potential for high-resolution in vivo imaging applications. Explain why equation 9 can provide the theoretical basis for such studies!

d) Wide-field single molecule fluorescence microscopy represents another fluorescence-based technique that allows for diffusion studies at the single molecule level. In this case, the square displacement r^2 of individual tracks of diffusing molecules is observed as observed over time. Which of the following two equations provide the proper relationship between r^2 and diffusion coefficient D? Justify your answer!

$$D = \frac{r^2}{4t_{lag}} \qquad\qquad D = \frac{\langle r^2 \rangle}{4t_{lag}}$$

$\langle r^2 \rangle$.....average value of r^2

3. In the case of a chemical reaction, the temperature-dependent change in Gibbs free energy is linked to the enthalpy change via the Gibbs-Helmholtz equation

$$\left[\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right)\right]_P = -\frac{\Delta H}{T^2} \tag{10}$$

(a) Derive equation 10 from the Gibbs free energy.

(b) Let's assume that the equilibrium constant of a chemical reaction K has been determined at one specific temperature and one would like to know the equilibrium constant at another temperature. The proper relationship is given by the van't Hoff equation

$$\left[\frac{\partial(\ln K)}{\partial\left(\frac{1}{T}\right)}\right]_P = -\frac{\Delta H^0}{R} \tag{11}$$

Derive equation 11 by starting from the temperature dependence of the Gibbs free energy under standard conditions ΔG^0!

(c) Assume that ΔH^0 remains constant between T_1 and T_2 characterized by K_1 and K_2, respectively. On the basis of equation 11, provide a relationship, which links both temperatures and equilibrium constants!

Periodic Classification of the Elements

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
1 H 1.00797																	2 He 4.0026
3 Li 6.939	4 Be 9.0122											5 B 10.811	6 C 12.01115	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.183
11 Na 22.9898	12 Mg 24.312											13 Al 26.9815	14 Si 28.086	15 P 30.9738	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.909	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.905	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (99)	44 Ru 101.07	45 Rh 102.903	46 Pd 106.4	47 Ag 107.870	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.9044	54 Xe 131.30
55 Cs 132.905	56 Ba 137.34	57 La* 138.91	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.980	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac† (227)															

Lanthanides	58 Ce 140.12	59 Pr 140.907	60 Nd 144.24	61 Pm (147)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.924	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.97
†*Actinides*	90 Th 232.038	91 Pa (231)	92 U 238.03	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (256)	103 Lw (257)

(Numbers in parentheses are the mass numbers of the most stable isotopes.)