

crib
3-3-07

March 2007 Analytical Cumulative Exam Question

generate a noisy data set

$$i := 0..5 \quad C_i := i \cdot 2 \cdot 10^{-6} \quad A_i := \text{round}(5.572 \cdot 10^4 \cdot C_i + \text{rnorm}(\text{length}(C), 0, 0.003842), i, 3)$$

$$C = \begin{pmatrix} 0 \\ 2 \times 10^{-6} \\ 4 \times 10^{-6} \\ 6 \times 10^{-6} \\ 8 \times 10^{-6} \\ 1 \times 10^{-5} \end{pmatrix} \quad A = \begin{pmatrix} -2 \times 10^{-3} \\ 0.114 \\ 0.219 \\ 0.332 \\ 0.45 \\ 0.558 \end{pmatrix}$$

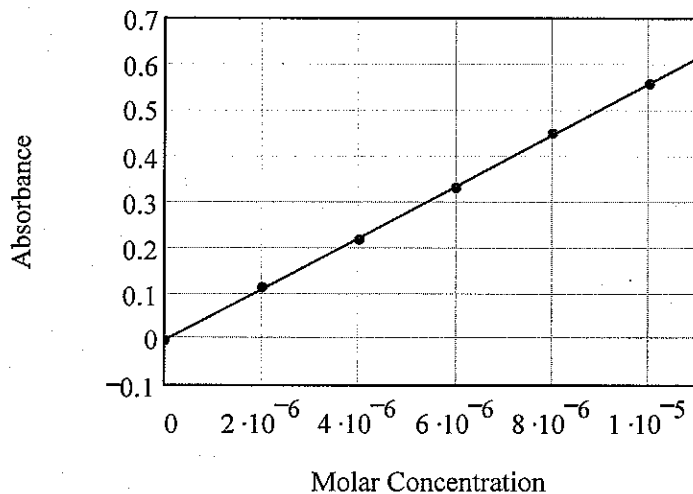
perform a least-squares fit to the data

$$N := \text{length}(A)$$

$$sA := \sum_i A_i \quad sC := \sum_i C_i \quad sAC := \sum_i (A_i \cdot C_i) \quad sC2 := \sum_i (C_i)^2$$

$$\Delta := N \cdot sC2 - sC^2 \quad a0 := \frac{sA \cdot sC2 - sAC \cdot sC}{\Delta} \quad a0 = -1.571 \times 10^{-3}$$

$$a1 := \frac{N \cdot sAC - sC \cdot sA}{\Delta} \quad a1 = 5.601 \times 10^4 \quad \text{regress}(z) := a0 + a1 \cdot z$$



error of the fit

$$s := \sqrt{\frac{1}{N-2} \cdot \left[\sum_i (A_i - a_0 - a_1 \cdot C_i)^2 \right]} \quad s = 3.297 \times 10^{-3}$$

sensitivity

Given by the slope of the calibration curve, and has units of absorbance per molarity.

$$a_1 = 5.601 \times 10^4$$

limit of detection

Given by a concentration yielding a signal ($A - a_0$) three times the noise level.

$$\frac{3 \cdot s}{a_1} = 1.766 \times 10^{-7}$$

coefficient errors

$$sa_0 := \sqrt{\frac{s^2}{\Delta} \cdot sC_2} \quad sa_0 = 2.386 \times 10^{-3}$$

95% confidence limits about the average of the intercept

$$df := N - 2$$

$$df = 4$$

$$\phi_1 := 1..6$$

$$t := qt(0.975, 4)$$

$$t = 2.776$$

$$\phi_1 = qt(0.975, \phi_1) =$$

1	12.706
2	4.303
3	3.182
4	2.776
5	2.571
6	2.447

$$a_0 - t \cdot sa_0 = -8.197 \times 10^{-3}$$

$$a_0 + t \cdot sa_0 = 5.054 \times 10^{-3}$$

The t-limits include zero, thus the intercept is statistically indistinguishable from zero.

F-test at 95% of s versus a specified value of $1 \cdot 10^{-3}$

$$\sigma := 1 \cdot 10^{-3} \quad \sigma^2 = 1 \times 10^{-6} \quad \text{a specified value has infinity degrees of freedom}$$

$$\frac{s^2}{\sigma^2} = 10.871 \quad \phi_2 := 10^4 \quad \text{use } 10^4 \text{ to mimic infinity}$$

$\phi_1 =$	$qF(0.95, \phi_1, \phi_2) =$
1	3.842
2	2.997
3	2.606
4	2.373
5	2.215
6	2.099

since the calculated F-parameter is larger than the table value for 4 degrees of freedom, the experimental standard deviation is larger than the manufacturer's specified value.

Answers to March 3rd Biochemistry Cume

1. What is the basic concept on which proteomics is based?

Answer. The basic idea in modern proteomics is to exploit the fact that the sequence of proteins is coded by gene sequence. This means that a DNA database of the genome of an organism can be used to predict 1) the primary structure of gene products 2) along with the cleavage fragments of a protein produced by enzymes such as trypsin that cleave proteins at specific amino acids. This makes it possible to compare experimental data derived with the genomic data base to experimental data from a mass spectrometer and see whether there is a match. It also allows one to determine the probable protein source of a protein fragment.

2. Mass spectrometry is of major importance in proteomics. Why are MS measurements inherently more important in determining the primary structure of proteins than those of any other type of analytical instrumentation?

Answer. As noted above, DNA databases allow one to predict polypeptide sequence, i.e. the specific amino acid sequence of proteins and their peptide cleavage fragments. Because each amino acid has a unique mass, with the exception of Leu and Ileu, the mass of tryptic peptides can be predicted along with the mass of peptides fragments produced in a tandem mass spectrometer through collision induced dissociation. This means that when a protein is either analyzed directly or peptide fragments of a protein are examined by mass spectrometry their mass can be determined and compared with predictions derived from a DNA database. Moreover, when the mass of multiple peptides is obtained together they provide a mass signature of a protein. The means that mass measurements provide a large body of data directly related to protein structure that can be confirmed by *in silico* analyses of DNA databases.

3. Mass spectral data generally only implies the structure of a polypeptide. It doesn't actually tell you the structure of the protein parent. Why or how could this be true? How could errors be made in predicting the structure of a protein from mass spectral data? What kind of errors could be made in assigning protein structure?

Answer. Errors could be made in a number of ways. When analyzing proteolytic fragments of a protein it is seldom the case that one sees all the peptides that theoretically could be derived from a protein. Even so it is generally assumed that if as few as two peptides from a protein are seen, the entire protein may be present. Unless one sees peptides from both ends of the protein, it could be that one is looking at a protein fragment, not the whole

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protein. This means that errors are being made when it is assumed that aspects of a protein are present unless they are actually seen. Moreover, there could be post-translational modifications (PTMs) in the missed peptides. Because DNA databases do not predict post-translational modifications, the proper structure is not being assigned if they are ignored.

Similar problems are encountered in top-down proteomics. PTMs increase the mass of proteins and can lead to the conclusion they are a different protein. Also multiple PTMs have the same mass as in glycoproteins.

Finally, mass spectral data does not allow the assignment of secondary and tertiary structure.

4. Quantification has been a problem in proteomics. Why is that? What are some of the ways that quantification has been achieved? What are the relative merits of the methods you have listed?

Answer. Staining is widely used for quantification in 2-D gel electrophoresis. The problem with staining is that it is of limited dynamic range, has an LOD of roughly 0.1 ng, and is often non-linear. The best dye is probably Sypro-ruby. A second approach is stable isotope coding of proteins according to sample origin. In the *in vivo* labeling method experimental samples are grown on heavy isotope containing nutrients, generally amino acids. During protein synthesis these heavy isotope precursors are incorporated into proteins. These heavy isotope coded samples are then mixed with un-labeled control (untreated) samples and examined by mass spectrometry. Quantification of the isotope ratio between isotopomers of peptides or proteins allows the relative concentration of proteins among samples to be determined. A similar strategy has been used *in vitro*. In this case peptides are globally derivatized *in vitro* according to sample origin with isotopically distinct labeling agents. Again they are mixed and analyzed by mass spectrometry to determine isotope ratio and relative concentration.

5. Describe some global ideas of methods for recognizing post-translational modifications in proteins.

Answer. The most widely used approach is to use an affinity selector that recognize a particular PTM. Lectins (glycoproteins and glycopeptides), boronate chromatography columns (glycoproteins and glycopeptides), immobilized metal affinity columns (phosphorylation), and antibodies (phosphorylation) have all been used with great success. Use of avidin to select biotinylated proteins and peptides has also been used to isolate oxidized proteins. Another approach is to look for the loss of particular PTM associated fragment ions from peptides and proteins during tandem MS.

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March 3, 2007

A. (a) Formal oxidⁿ states and dⁿ configur^{ns}

(i) $TiO(acac)_2$	Ti(IV) d^0
(ii) $Ti(acac)_3$	Ti(III) d^1
(iii) $[VCl_2(H_2O)_4]^+$	V(III) d^2
(iv) $[MnCl_4]^{2-}$	Mn(II) d^5
(v) $Cr[N(SiMe_3)_2]_3$	Cr(III) d^3
(vi) $[Fe(CO)_6]^{4-}$	Fe(II) d^6
(vii) $Ni(CO)_4$	Ni(0) d^{10}
(viii) $(\eta^5-C_5H_5)_2Fe$	Fe(II) d^6
(ix) $[(\eta^6-C_6Me_6)TiCl_3]^+$	Ti(IV) d^0
(x) $[V(CO)_6]^-$	V(-I) d^6

(b) Electron Counts

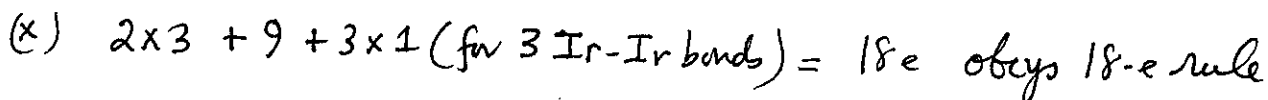
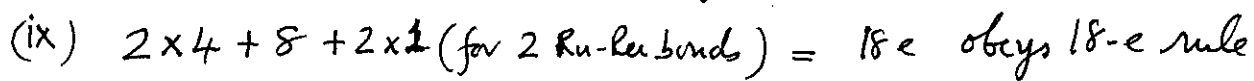
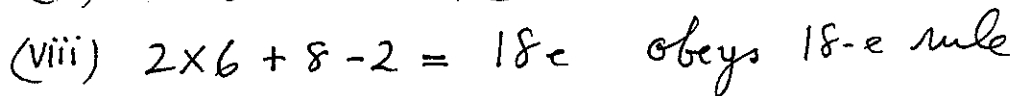
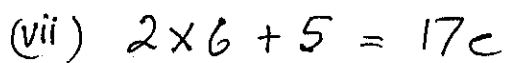
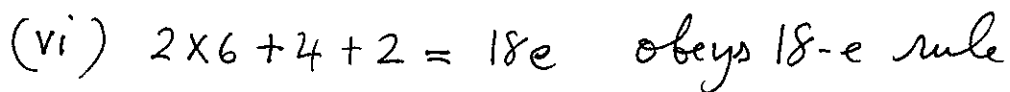
(i) $2 \times 5 + 5 = 15e$

(ii) $2 \times 5 + 8 = 18e$ obeys 18-e rule

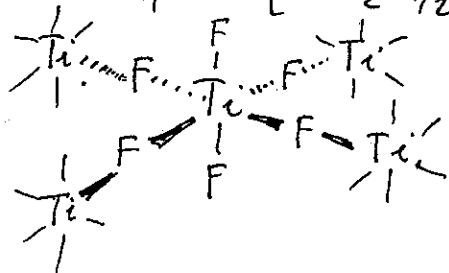
(iii) $2 \times 6 + 6 = 18e$ obeys 18-e rule

(iv) $2 \times 5 + 2 \times 1 + 4 = 16e$

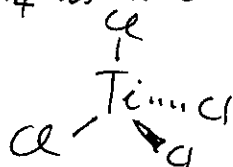
(v) $2 \times 5 + 2 \times 2 + 4 = 18e$ obeys 18-e rule



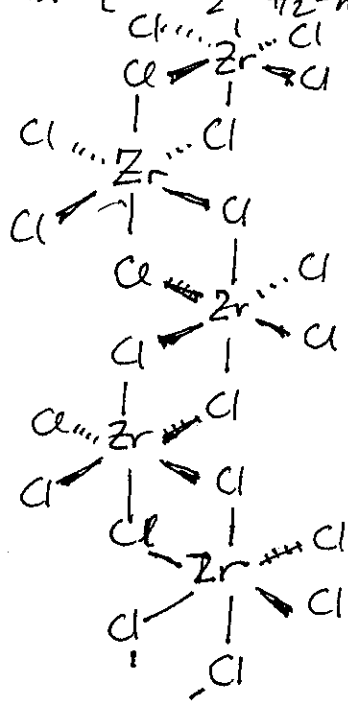
B. (a) TiF_4 is $[TiF_2F_4/2]_n$ corner-linked octahedron

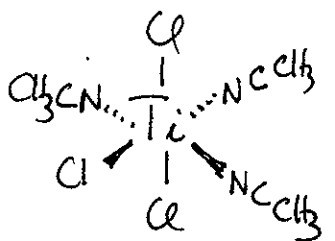
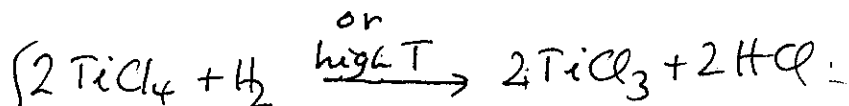
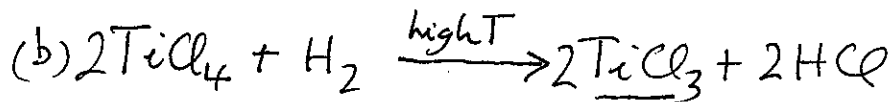


(b) $TiCl_4$ is a tetrahedral monomer

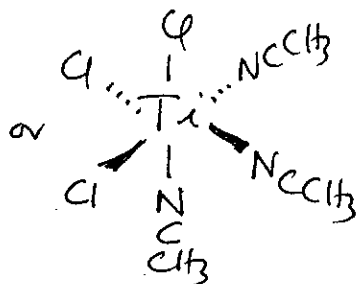


(c) $ZrCl_4$ is $[ZrCl_2Cl_4/2]_n$ polymeric cis-bridged zig-zag chains

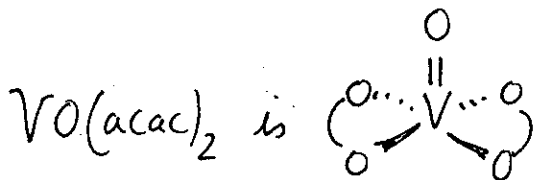
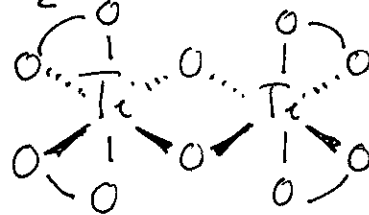
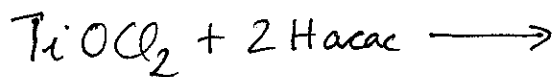
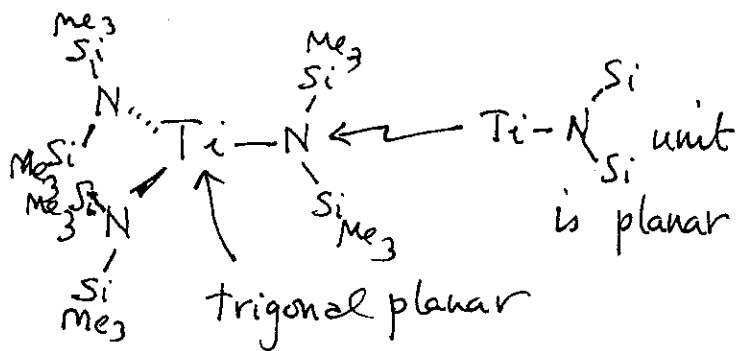
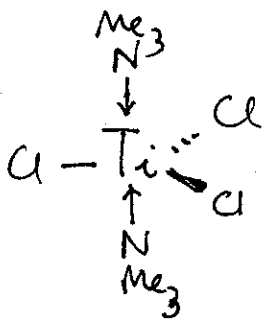


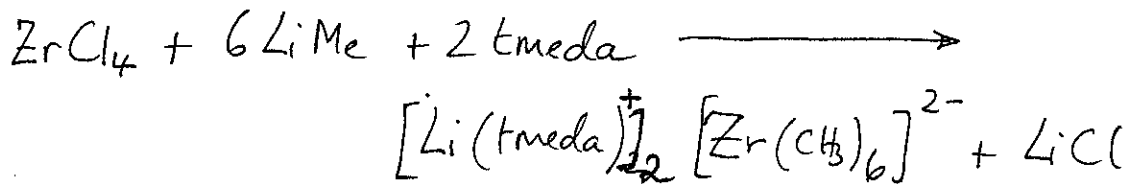
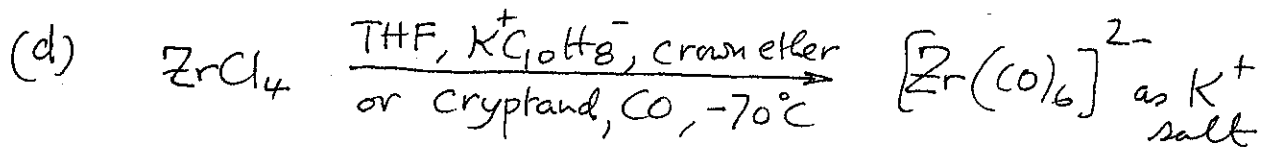


mer-isomer

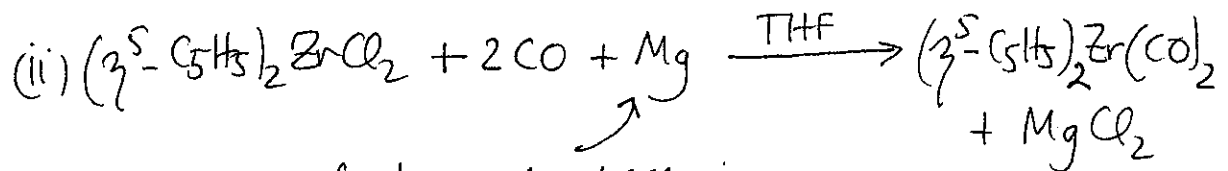
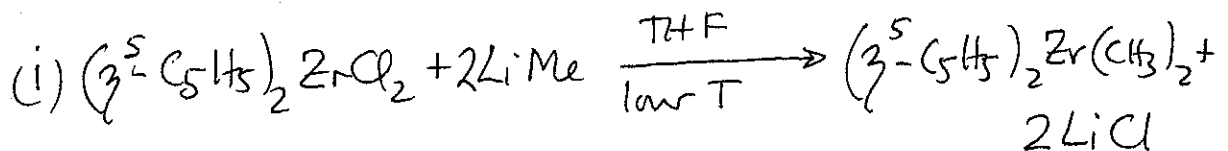
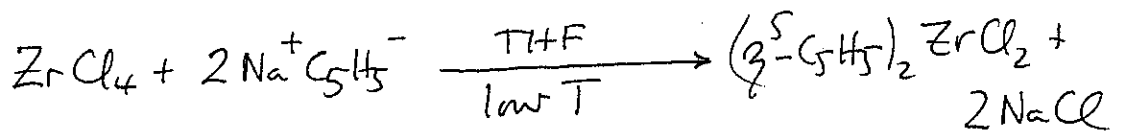


fac-isomer

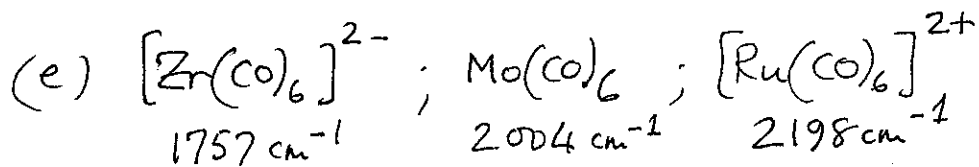
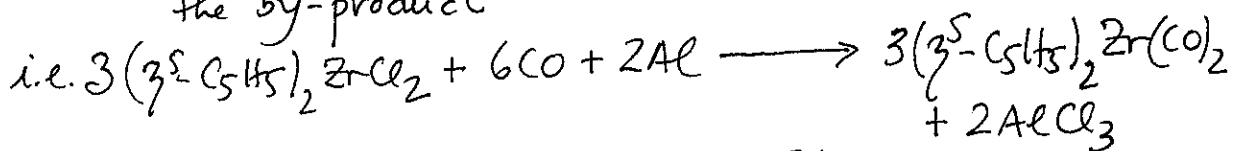




(tmeda = $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$)



Al can also be used; AlCl_3 is the by-product



Isoelectronic series - all are 18-electron species

$\text{M}(d_{\pi}) \rightarrow \text{CO}(\pi^*)$ back bonding decreases $\text{Zr} > \text{Mo} > \text{Ru}$ as the $+ve$ charge increases. The greater the π -back bonding the lower the $\nu(\text{CO})$ frequency.

No Organic crib available

March 3, 2007

Written by Professor Savinov

1.

Solutions to
Physical Cume Exam
March 3, 2007

Note: Gas constant $R = 8.31451 \text{ J K}^{-1} \text{ mol}^{-1}$

Exam

1. This problem involves the calculation of equilibrium constants $K_{\text{eq}}(T)$ for the reaction



in a range $T \geq 298.15\text{K}$ and $T \leq 450\text{K}$. You will require the two sheets at the end of the exam for data. Note from the first sheet I_2 is a solid until $T = 386.85\text{K}$ and then forms a liquid until $T = 457.4\text{K}$. Also as indicated in (1) H_2 and HI are gases over the whole T range.

You will need the following additional information:

- (i) For an arbitrary molar state function $X \equiv X_m$ and a generic reaction



ΔX for the reaction is defined as

$$\Delta X \equiv \nu_C X_C + \nu_D X_D - \nu_A X_A - \nu_B X_B \quad 3.$$

- (ii) For the reaction of (2)

$$\Delta G^0(T) = -RT \ln K_{\text{eq}}(T) \quad 4.$$

where $0 \equiv P = 1\text{bar}$. (Recall $G = G_m \equiv \mu$).

- (iii) For the reaction of (2)

$$\frac{d \ln K_{\text{eq}}(T)}{dT} = \frac{\Delta H^0(T)}{RT^2} \quad 5.$$

Solve the following three problems

- (a) Compute K_{eq} (298.15K)
- (b) Compute K_{eq} (380K)
- (c) Compute K_{eq} (450K)

State all assumptions and show all your work. Make approximations required by the data available (that is do all calculations using only the data available).

Iodine

Physical Cume Exam
March 3, 2007

From Wikipedia, the free encyclopedia

Iodine (IPA: /ˈaɪə(ʊ),dɪˈoʊn/, Greek: *iodēs*, meaning "violet"), is a chemical element in the periodic table that has the symbol **I** and atomic number 53. Chemically, iodine is the least reactive of the halogens, and the most electropositive halogen after astatine. Iodine is primarily used in medicine, photography and dyes. It is required in trace amounts by most living organisms.

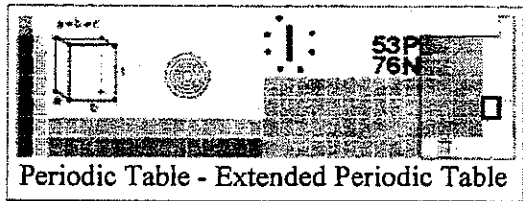

As with all other halogens (members of Group VII in the Periodic Table), iodine forms diatomic molecules, and hence, has the molecular formula of I_2 .

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Occurrence on earth

Iodine naturally occurs in the environment chiefly as dissolved iodide in seawater, although it is also found in some minerals and soils. The element may be prepared in an ultrapure form through the reaction of potassium iodide with copper(II) sulfate. There are also several other methods of isolating this element. Although the element is actually quite rare, kelp and

53	tellurium ← iodine → xenon					
Br ↑ I ↓ At						
General						
Name, Symbol, Number	iodine, I, 53					
Chemical series	halogens					
Group, Period, Block	17, 5, p					
Appearance	violet-dark gray, lustrous 					
Atomic mass	126.90447(3) g/mol					
Electron configuration	[Kr] 4d ¹⁰ 5s ² 5p ⁵					
Electrons per shell	2, 8, 18, 18, 7					
Physical properties						
Phase	solid					
Density (near r.t.)	4.933 g·cm ⁻³					
Melting point	386.85 K (113.7 °C, 236.66 °F)					
Boiling point	457.4 K (184.3 °C, 363.7 °F)					
Critical point	819 K, 11.7 MPa					
Heat of fusion	(I ₂) 15.52 kJ·mol ⁻¹					
Heat of vaporization	(I ₂) 41.57 kJ·mol ⁻¹					
Heat capacity	(25 °C) (I ₂) 54.44 J·mol ⁻¹ ·K ⁻¹					
Vapor pressure (rhombic)						
<i>P</i> /Pa	1	10	1001	k	10 k	100 k
at <i>T</i> /K	260	282	309	342	381	457
Atomic properties						
Crystal structure	orthorhombic					
Oxidation states	±1, 5, 7 (strongly acidic oxide)					

Compound	$H_m^0(298.15K),$ in kJ/mol	$\mu^0(298.15K),$ in kJ/mol	$S_m^0(298.15K),$ in J/(mol-K)]
HI(g)	26.5	1.7	114.7
H ₂ (g)	0	0	130.68
I ₂ (s)	0	0	116.14

SOLUTIONS

1a. Compute $K_{eq}(298.15\text{K})$ for the reaction of Eq. (1).

Eq. (4) when evaluated for $T = 298.15\text{K}$ may be written as

$$K_{eq}(298.15\text{K}) = \exp\left[\frac{-\Delta G^\circ(298.15\text{K})}{(298.15\text{K})R}\right] \quad 6.$$

From Eqs. (1)–(3) with $X = G \equiv G_m = \mu$, $\Delta G^\circ(298.15\text{K})$

may be expressed as

$$\Delta G^\circ(298.15\text{K}) = 2\mu_{\text{HI}(g)}^\circ(298.15\text{K}) - \mu_{\text{H}_2(g)}^\circ(298.15\text{K}) - \mu_{\text{I}_2(s)}^\circ(298.15\text{K}). \quad 7.$$

Using the Table on p. 3 and Eq. (7) one finds

$$\Delta G^\circ(298.15\text{K}) = 2(1.7) - 0 - 0 = 3.4 \text{ kJ}\cdot\text{mol}^{-1} \quad 8.$$

Combining Eqs. (6) and (8) and using $R = 8.31451 \times 10^{-3} \text{ kJ}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$,

Eq. (6) gives

$$K_{eq}(298.15\text{K}) = \exp\left[\frac{\overbrace{-3.4 \text{ kJ}\cdot\text{mol}^{-1} \times 10^3}^{\text{dimensionless}}}{(298.15\text{K})(8.31451) \text{ kJ}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}\right] \quad 9.$$

or

$$\boxed{K_{eq}(298.15\text{K}) = 0.2537.} \quad 10.$$

b. Compute $K_{eq}(380\text{K})$ for the reaction of Eq. (1).

Note that $T=380\text{K}$, I_2 is still a solid - melting occurs at the higher T of 386.15K . Thus at 380K it is legitimate to make the approximation that

$$H_{\text{I}_2}(380\text{K}) = H_{\text{I}_2(\text{s})}(380\text{K}) \approx H_{\text{I}_2(\text{s})}(298.15\text{K}) \quad (11a)$$

We also make analogous approximations for the other substances in Eq. (1); i.e.

$$H_{\text{H}_2(\text{g})}(380\text{K}) \approx H_{\text{H}_2(\text{g})}(298.15\text{K}) \quad (11b)$$

and

$$H_{\text{I}_2(\text{g})}(380\text{K}) \approx H_{\text{I}_2(\text{g})}(298.15\text{K}). \quad (11c)$$

There are no phase transitions for H_2 and I_2 in the specified range $298.15\text{K} \leq T \leq 457.4\text{K}$ so Eqs. (11b-c) are natural simplest approximations in that range.

Using Eqs. (1-3) and Eq. (11), Eq. (3) for $X = H^\circ(380\text{K})$

has the following approximate form

$$\Delta H^\circ(380\text{K}) \approx \Delta H^\circ(298.15\text{K}) = 2 H_{\text{HI}(\text{g})}^\circ(298.15\text{K}) - H_{\text{H}_2(\text{g})}^\circ(298.15\text{K}) - H_{\text{I}_2(\text{s})}^\circ(298.15\text{K}) \quad (12)$$

Using the Table on p. 3 and Eq. (10) one finds

$$\Delta H^\circ(380\text{K}) \approx 2(26.5) - 0 - 0 = 53.0 \text{ kJ}\cdot\text{mol}^{-1} \quad 13$$

However integrating the van't Hoff Eq. (15) from 298.15K to 380K, and assuming in that sense that $\Delta H^\circ(T) \approx \Delta H^\circ(298.15\text{K})$, as in Eq. (12), gives

$$\ln K_{\text{eq}}(380\text{K}) = \ln K_{\text{eq}}(298.15\text{K}) + \frac{\Delta H^\circ(298.15\text{K})}{R} \left(\frac{1}{298.15\text{K}} - \frac{1}{380\text{K}} \right) \quad 14.$$

Using Eqs. (10) and (13) and the value for R given on

p. 1 gives

$$\ln K_{\text{eq}}(380\text{K}) = \ln[0.2537] + \frac{53.0 \text{ kJ}\cdot\text{mol}^{-1}}{8.31451 \times 10^{-3} \text{ kJ}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}} \left[\frac{1}{298.15\text{K}} - \frac{1}{380\text{K}} \right] \quad 15.$$

Evaluating Eq. (15) gives

$$\boxed{\ln K_{\text{eq}}(380\text{K}) = 3.2335 \quad \text{and} \quad K_{\text{eq}}(380\text{K}) = 25.3682} \quad 16.$$

So $K_{\text{eq}}(T)$ increases substantially as T increases from 298.15K to 380K.

C. Compute $K_{eq}(450K)$ for the reaction of Eq. (1)

One might think that one could use Eq. (14) with 380K replaced by 450K. This is not the case since at 380 I₂ is a solid while at 450K it is a liquid. As noted on p. 1, the melting phase transition occurs for P=1 bar at T=386.85 K. We will denote by T₋ the temperature infinitesimally below 386.85 K and by T₊ the temperature infinitesimally above 386.85 K. At T₋ I₂ = I₂(s) but at T₊ I₂ = I₂(l).

Next we will: (i) compute $K_{eq}(T_-)$ from Eq. (14) with 380K replaced by T₋; (ii) we will compute the change of $K_{eq}(T_-)$ due to the melting transition to get $K_{eq}(T_+)$; (iii) then we will compute the change in ΔH° from the value in Eq. (13) due to the melting transition. We will rename the old value of $\Delta H^\circ = 53.0 \text{ kJ}\cdot\text{mol}^{-1}$ ΔH_s° (for I₂(s)) and the new value of $\Delta H^\circ \Rightarrow \Delta H_l^\circ(T_+)$ will be named ΔH_l° (for I₂(l)). We will then compute $K_{eq}(T)$ from an equation similar to Eq. (14); namely,

$$\ln K_{eq}(450K) = \ln K_{eq}(T_+) + \frac{\Delta H_l^\circ(386.85)}{R} \left(\frac{1}{386.85K} - \frac{1}{450K} \right) \quad 17.$$

Like Eq. (14), Eq. (17) may be derived from the van't Hoff Eq. (5) if it is assumed that, like $\Delta H_s^\circ(T) = \Delta H^\circ$, ΔH_l° is independent of T.

Lets start

Step (i). Compute $K_{eq}(T_-)$ by making the replacement 380K \rightarrow the I₂ melting temperature = 386.85K in Eq. (16). This gives (after cancelling units)

$$\ln K_{eq}(T_-) = \ln [0.2537] + \frac{53.0}{8.31451 \times 10^{-3}} \left[\frac{1}{298.15K} - \frac{1}{386.85K} \right] \quad 18.$$

Evaluating Eq. (17) gives (cf. Eq. [16])

$$\ln K_{eq}(T_-) = 3.5305 \quad \text{and} \quad K_{eq}(T_-) = 34.1423. \quad 19.$$

Step (ii)

From Eq. (4),

$$K_{eq}(T_-) = \exp \left[-\frac{\Delta G^\circ(T_-)}{RT_-} \right] = \exp \left[-\frac{\Delta G^\circ(T_-)}{R(386.85K)} \right] \quad (20a)$$

and

$$K_{eq}(T_+) = \exp \left[-\frac{\Delta G^\circ(T_+)}{RT_+} \right] = \exp \left[-\frac{\Delta G^\circ(T_+)}{R(386.85K)} \right] \quad (20b)$$

From Eqs. (20) any change in K_{eq} due to melting arises from a corresponding change in ΔG° at 386.85 K. But from Eqs. (1) and (3)

$$\begin{aligned} \Delta G^\circ(T_-) \equiv \Delta G^\circ_s(386.85K) &= 2\mu_{HI(g)}^\circ(386.85K) - \mu_{H_2(g)}^\circ(386.85K) \\ &\quad - \mu_{I_2(s)}^\circ(386.85K) \quad 21a \end{aligned}$$

and

$$\begin{aligned} \Delta G^\circ(T_+) \equiv \Delta G^\circ_l(386.85K) &= 2\mu_{HI(g)}^\circ(386.85K) - \mu_{H_2(g)}^\circ(386.85K) \\ &\quad - \mu_{I_2(l)}^\circ(386.85K) \quad 21b \end{aligned}$$

However from Eqs. (21), $\Delta G^\circ(T_+) \neq \Delta G^\circ(T_-)$ only if $\mu_{I_2(s)}^\circ(386.85) \neq \mu_{I_2(l)}^\circ(386.85)$. However since l and s I_2 are in equilibrium at the melting temperature 386.85 K, it follows that (see any P. Chem. book)

$$\mu_{I_2(s)}^\circ(386.85K) = \mu_{I_2(l)}^\circ(386.85K) \quad 22.$$

and, hence, from Eqs. (19) - (22)

$$K_{eq}(T_+) = K_{eq}(T_-) = K_{eq}(386.85K) = 34.1423. \quad 23.$$

Summarizing: Eq. (23) states that the melting at 386.85 K

does not change $K_{eq}(T)$ at $T = 386.85$ K.

Step (iii). In analogy to Eqs. (21)

$$\Delta H^\circ(T_-) \equiv \Delta H_s^\circ(386.85 \text{ K}) = 2H_{HI(l)}^\circ(386.85 \text{ K}) - H_{H_2O(l)}^\circ(386.85 \text{ K}) - H_{I_2(s)}^\circ(386.85 \text{ K}) \quad 240$$

and

$$\Delta H^\circ(T_+) \equiv \Delta H_r^\circ(386.85 \text{ K}) = 2H_{HI(g)}^\circ(386.85 \text{ K}) - H_{H_2O(g)}^\circ(386.85 \text{ K}) - H_{I_2(l)}^\circ(386.85 \text{ K}) \quad 246$$

In contrast to Eq. (22), $H_{I_2(s)}^\circ(386.85 \text{ K}) \neq H_{I_2(l)}^\circ(386.85 \text{ K})$.

Rather (all H's for 386.85 K)

$$H_{I_2(l)}^\circ = H_{I_2(s)}^\circ + [H_{I_2(l)}^\circ - H_{I_2(s)}^\circ] = H_{I_2(s)}^\circ + \Delta H_{fus, I_2}^\circ \quad 25$$

where the enthalpy (or heat) of fusion $\Delta H_{fus, I_2}^\circ \equiv H_{I_2(l)}^\circ - H_{I_2(s)}^\circ$

is given in the Physical Properties box on exam p. 2 as

$$\Delta H_{fus, I_2}^\circ = 15.52 \text{ kJ} \cdot \text{mol}^{-1} \quad 26$$

From Eqs. (24) - (26),

$$\Delta H_r^\circ(386.85) = \Delta H_s^\circ(386.85) - 15.52 \text{ kJ} \cdot \text{mol}^{-1}$$

But given our assumption that $\Delta H^\circ \equiv \Delta H_s^\circ$ is T-independent, from Eq. (23)

$$\Delta H^\circ (386.85) \equiv 53.0 \text{ kJ-mol}^{-1} - 15.52 \text{ kJ-mol}^{-1}$$

or

$$\Delta H^\circ (386.85 \text{ K}) = 37.5 \text{ kJ-mol}^{-1}$$

27.

Step (iv). Compute $K_{eq}(450 \text{ K})$

Inserting Eqs. (23) and (25) into Eq. (10) to give (cancel units)

$$\ln K_{eq}(450 \text{ K}) = \ln [34.1423]$$

$$+ \frac{37.5}{8.31451 \times 10^{-3}} \left[\frac{1}{386.85} - \frac{1}{450} \right]$$

28.

Evaluating Eq. (28) gives the result requested for part (c)

$$\ln K_{eq}(450 \text{ K}) = 5.1666$$

$$K_{eq}(450 \text{ K}) = 275.3177.$$