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胡　萍　余少文　编著

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前　言

仪器分析一直是我国高校化学专业的基础课，但随着科技的不断飞速发展及各学科的交叉渗透，仪器分析越来越受到重视并逐渐扩展应用到相关领域，成为目前高校化学系、生物系、医药系、食品系等必修课。本书正是适应这一形势之需要，同时配合仪器分析的课程建设与教学改革而编写，尤其是在笔者近年进行的“考试科学化与试题质量评估”、“多媒体组合之电化教学实践”、“课堂教学中形成性练习的研究”等研究课题的教学实践中，经过不断使用、修改与完善，对许多习题在难度和区分度等评估指标亦经过反复实践与检验，故本书作为配套教材在仪器分析教学有关形成性练习、课堂测验、试题库建立和标准化考试等应用方面取得显著效果。

本书的编写特点有以下几方面：

1. 知识点突出：各章均按相应教学内容的各主要知识点有针对性地一一分类列出，充分考虑到了教与学的目的性与实用性。

2. 习题量较大：全书对应多种仪器分析方法，各有习题100～300道，合计有两千多道题，并附有部分答案。

3. 题型多样化：有选择题、是非题、填充题、计算题和问答题等，可以对各知识点相应的内容从不同角度与层次加深理解与掌握。

4. 中英文兼顾：除中文习题外，每章还有英文题。

本书可作为仪器分析课程的教学参考书，也可供有关行业的分析工作者参考。

本书编写过程中参考了有关资料，吸收了部分有代表性的习题，为此谨向有关同志致谢。

因编者水平有限，书中难免有不妥与不足之处，恳请读者予以批评与指正。

编　者

一九九五年十月一稿

一九九八年十月二稿

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1-3　吸收光谱与发射光谱在原理上有何区别?

1-4　何谓转动、振动光谱?写出这两种光谱的波长范围,并说明这两种光谱能给出物质分子的哪些信息。

1-5　热辐射是否可用于结构分析?为什么?

1-6　共振发光、荧光发射、磷光发射有何异同点?

1-7　解释下列名词:

(1) 单重态与三重态;　　(2) 原子荧光与分子荧光;

(3) 选择跃迁与禁阻跃迁;　　(4) 激发电位与共振电位。

1-8　真空中一电磁辐射的波长为 275 nm。试确定该辐射的频率和周期,并求算该辐射中每个光子所具有的能量。

1-9　一具有 589.3 nm 波长的辐射在铁铝氧石中的速度为 1.90×10^{8} m·s^{-1}。计算在 589.3 nm处铁铝氧石的折射率。

1-10　干燥空气 ($n=1.00\,028$) 中一电磁辐射具有 460.0 nm 的波长。试确定该辐射的频率及辐射中一个光子所具有的能量。

1-11　计算 15 ℃下,一具有 4.708×10^{14}Hz 频率的辐射在真空及在熔凝石英 ($n=1.467$) 中的波长。

1-12　计算具有 589 nm 波长的辐射在空气中每个光子的能量。

1-13　在 434 nm 下,轻质燧石玻璃的折射率为 1.594。试计算一辐射穿过该玻璃时,每一个光子所具有的能量。

1-14　某种玻璃的折射率为 1.7 000,求光在此玻璃介质中的传播速度。

(答: 1.76×10^{10} cm·s^{-1})

1-15　辐射通过空气与玻璃界面时,其反射损失大约有多少?　　(答: 4%)

1-16　对下列单位进行换算:

(1) 0.15 nm X 射线的波数 (cm^{-1});　　(答: (1) 6.66×10^{7}

(2) 670.7 nm 锂线的频率 (Hz);　　(2) 4.47×10^{14}

(3) 3 300 cm^{-1}波数的波长 (nm);　　(3) 3 030

(4) Na 588.995 nm 相应的能量 (eV)。　　(4) 2.11)

1-17 计算下列辐射的频率（以 Hz 为单位）和波数（以 cm^{-1}为单位）。

（1）波长为 0.9 nm 的单色 X 射线；

（2）589.0 nm 的钠 D 线；

（3）12.6 μm 的红外吸收峰；

（4）波长为 200 cm 的微波辐射。

能级跃迁

1-18 原子中电子的运动状态用什么来描述?什么是电子轨道?电子轨道由哪些量子数规定？它们可取哪些数值?

1-19 计算氢原子从基态跃迁到第一激发态时，光谱线的频率和波长。

（实测值 γ= 3 225.9 cm，λ=121.5 664 nm)。

1-20 已知钠原子从基态跃迁到 $3p$ 态的激发电位为 2eV,计算在 3 000K 时处于 $3p$ 激发态的钠原子数对基态原子数之比。

1-21 写出下列各种跃迁所需的能量范围（eV）：

（1）原子内层电子跃迁；	（答：	（1）$1.2\times10^{2}\sim1.2\times10^{6}$
（2）原子外层电子跃迁；		（2）$6.2\sim1.7$
（3）分子的电子跃迁；		（3）$6.2\sim1.7$
（4）分子振动能级跃迁；		（4）$0.5\sim0.02$
（5）分子转动能级跃迁。		（5）$2\times10^{-2}\sim4\times10^{-7}$）

光谱项

1-22 阐明光谱项符号和能级图的意义。

1-23 用光谱项符号写出 Mg 285.2 nm（共振线）的跃迁。 （答：$3^1S_0\rightarrow3^1P_1$）

1-24 光谱项 3^2D，$3^2P_{\frac{1}{2}}$，$4S_{\frac{3}{2}}$中各符号都代表什么意义?

1-25 推求 $2S$、$2P$、$2D$、$2F$ 和 $3S$、$3P$、$3D$、$3F$ 的 J 值。

1-26 试推求基态钾原子和激发态 K $(4p)^1$、K $(4d)^1$及 K $(4f)^1$ 的光谱项，画出对应的能级图，指出哪些能级之间能发生跃迁。

1-27 试推求基态锌原子和激发态锌原子 $(4s)^1$ $(4p)^1$、$(4s)^1$ $(4d)^1$ 和 $(4s)^1$ $(4f)^1$ 的光谱项，画出对应的能级图，将能发生跃迁的能级之间用直线联接起来。

1-28 Li 原子的基态项为 $2s$。当把 Li 原子激发到 $3p$ 态后，问当 Li 从 $3p$ 激发态向低能级跃迁时可能产生哪些谱线（不考虑精细结构）?

1-29 在碱金属原子中，当主量子数相同时，光谱项数值受何因素的影响?

1-30 原子中能够有下列量子数相同的最大电子数是多少?

A. n、l、ml；　B. n、l；　C. n。

1-31 在氢原子、碱金属原子和复杂原子中角量子数 l 对能级的影响是否相同，请简要说明。

1-32 已知巴尔末线系的谱线波长（nm）为：656.279，486.133，434.047，410.174 试计算里德堡常数的值。

1-33 试计算 H 和 D 的折合质量。从而计算与 H 光谱中波长为 656.279（nm）的谱线相对应的 *D* 光谱谱线的波长。

1-34 下述哪种跃迁不能产生，为什么？

A. $3^1S_0 \rightarrow 3^1P_1$； C. $3^1S_0 \rightarrow 3^1D_2$；

B. $3^3P_2 \rightarrow 3^3D_3$； D. $4^3S_1 \rightarrow 4^3P_1$； （答：$3^1S_0 \rightarrow 3^1D_2$）

1-35 一个一级干涉滤色器使用了折射率为 1.512 的透明胶片，它可让 528 nm 的辐射通过。计算此滤色器的厚度。

1-36 如果 678 nm 的一级辐射可通过一干涉滤色器，试确定能通过该滤色器的二、三、四级辐射的波长。

1-37 在有单色器的光谱仪上加滤光片能起什么作用？

1-38 用一绿色滤光片和一橙色截止式滤光片能否得到波长范围为 550～600 nm 的透过光？为什么？

棱镜

1-39 单色辐射进入一个等边三角形棱镜，其入射角度为恰使在棱镜中通过的路线与底边平行。棱镜的折射率为 1.57。计算该辐射入射及出射棱镜的角度。

1-40 若棱镜的两底角各为 45°，而顶角为 90°，重复 1-39 题的计算。

1-41 辐射从一种折射率为 1.14 的介质打到折射率为 2.08 的另一种介质，如果入射角为 38.2°，计算折射角。

衍射光栅

1-42 一块反射型衍射光栅含有的刻槽密度为 2 125 条/mm。杂色辐射的入射角为 52.5°。试确定在 10.5°的角度上产生衍射的波长。

1-43 现需设计一个在入射角为 45.0°时，于 15.0°处能对 355 nm 的一级辐射产生色散的反射型衍射光谱。试确定光栅上每毫米应有的刻槽数及槽距。

1-44 填补下列反射光栅所缺少的数据：

光栅	光栅常数（条/mm）	衍射波长（nm）	反射角 $\overset{\circ}{\theta}$
A		500	26.4
B	1 180		8.1
C	1 184	300	
D	4 000	400	13.7
E	1 180		17.2
F	1 180	600	

色散率及分辨率

1-45 试确定可分离中心分别位于 573.5 nm 及 569.8 nm 的两个相邻峰的仪器的分辨率。在仪器的焦面上两峰分离的间距为 2.1 mm，计算该仪器的色散率及线性倒数色散率。

1-46 一使用反射型衍射光栅的特殊单色器，对中心分别位于 25.6 μm 及 27.3 μm 的两峰，在仪器焦面上分离的间距为 1.35 mm，试确定仪器的线性倒数色散率。

1-47 一单色器具有 35.00 nm 的分辨率。如果在 623.5 nm 处观察到一个光谱峰，那么使用该仪器则能分辨较此峰能量低的下一个峰的波长是多少？

1-48 一光栅单色仪，其倒线色散率为 1.6 nm/mm，分辨率为 0.6 nm，试计算其狭缝宽度。

1-49 国产 W-100 型光栅摄谱仪光栅的宽度为 60 mm，其光栅常数为 600 条/mm，计算该仪器一级光谱的理论分辨率。如改用棱镜，要达到此分辨率，则棱镜的底边长应达多少？

1-50 某一光栅摄谱仪，光栅的宽度为 60 mm，其光栅常数为 600 条/mm。计算一级光谱的理论分辨率。若将铁光谱的 309.990 nm，309.997 nm 线对分开，理论上应用哪一级光谱？

英文题

1-51 Calculate the period of electromagnetic radiation with $\lambda = 4.0\times10^3$ cm.

1-52 What is the frequency of green light with a wavelength of 500 nm?

1-53 Find the energy of the photons which corresponds to light of frequency 3.0×10^{15} s^{-1}.

1-54 Find the frequency of light which corresponds to photons of energy 5.0×10^{-12}J.

1-55 From the equation $E = h\nu$ and $\lambda\nu = c$, formulate an equation which relates energy to wavelength.

1-56 What is the energy of photons with a wavelength equal to 0.05 nm?

1-57 Show that $\bar{\nu}$ is proportional to energy.

1-58 What is the wavenumber for light with a wavelength of 400nm?

1-59 What is the energy of photons which have a wavenumber of $2.5\times10^{-5}cm^{-1}$?

1-60 In what region of the electromagnetic radiation will the following wavelengths be located?

A. 10 μm B. 0.8 μm (micrometer) ($1\mu m = 10^{-6}$ m)

C. 100 nm D. 10 nm

1-61 In what region of the electromagnetic radiation will the following wavenumbers be located?

A. 983 cm^{-1} B. 3.0×10^4 cm^{-1}

C. 5.0 cm^{-1} D. 8.7×10^4 cm^{-1}

1-62 Arrange the following regions of light in order of increasing energy.

A. x-ray B. visible

C. ultraviolet D. infrared

1-63 Convert each of the following quantities used to describe eleactromagnetic waves to wavelength (in vacuum) in meters.

A. 500 nm (in vacuum) B. 1 000K

C. 500 nm in a medium with n=1.4 D. 10^{15}Hz

1-64 Complete the following table.

Frequency	Transition energy		Spectral region
	Joules	Electron Volts	
8/		0.5	
9/3×10^{10}			
10/	1.6×10^{-19}		

1-65 What happens to the light waves missing from the spectrum given by an atom or molecule?

1-66 Each different type of atom and molecule interacts with light in its own characteristic way. What effect will this have on the absorption spectrum of different type of atoms and molecules?

1-67 An atom interacts with light by absorbing amount of energy equivalent to a given wavelength of light. If an atom has a spectral line at 400 nm, what energy has this atom absorbed?

1-68 An atom is known to absorb energy of 3.0×10^{-19}J. At what wavelength (in nm) would there be a spectral line in the spectrum of this atom?

1-69 An atom is known to absorb energy equal to 5.0×10^{-19}J. At what wavenumber would there be an absorption line in the spectrum of this atom?

1-70 Below is an energy diagram which represents the four lowest energy levels of an atom:

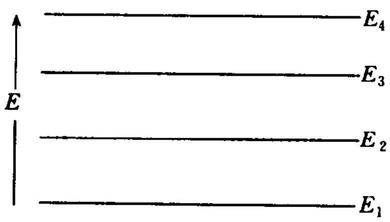

Figure 1-1

If an atom is in its lowest energy state, which level represents the energy of the atom?

1-71 What happens to the energy of the atom as it is excited from E_1 to E_2 and to E_3, etc.

1-72 What must happen before the atom can be excited from E_1 to E_2?

1-73 Write an expression for the amount of energy necessary to excite the atom from the first to the second energy level.

1-74 The energy necessary to excite the atom from one energy level to another is called a quantum of energy (a distinct amount). Why wouldn't intermediate values of energy be absorbed?

1-75 A transition from one energy level to another is indicated by use of an arrow. Draw on the diagram of figure 1-1 arrows to represent the three transitions that this an could undergo starting from its lowest level.

1-76 Electromagnetic radiation can interact with atoms and molecules to supply the quanta of energy necessary to cause transitions to higher energy levels. Account for the missing wavelengths of light present in the absorb spectrum of an atom or a molecule.

1-77 Give an expression which relates the energy of absorption to the wavelength of light absorbed in the process.

1-78 What factor determines the wavelength of light absorbed in a spectrum?

1-79 What explanation would account for the fact that the absorption spectrum for each kind of atom and molecule is unique?

1-80 Consider the transitions represented in 32. Which transition would give rise to absorption of light of longest wavelength?

1-81 For the diagram shown in 32, which transition would cause absorption of light with the largest wavenumber?

1-82 In the diagram of figure 1-1, assume that the difference in energy between the E_2 and E_1 levels is 6.0×10^{-18}J. What is the wavelength of light in nm needed to accomplish this transition?

1-83 Kinetic energy is given by the equation

$$E_k=\frac{1}{2}m^2$$

where m is the mass of the moving body and is its velocity. As the velocity of a molecule increases, what happens to its transitional energy?

1-84 As temperature increases, what happens to the average velocity of atoms and molecules?

1-85 What happens to the kinetic energy as temperature increases?

1-86 The relationship between average translational kinetic energy. E_k, for an atom or molecule and the temperature on the absolute scale. T is given by the equation

$$E_k=\frac{3}{2}kT$$

where k is a constant equal to 1.38×10^{-23}J/k (where k is the symbol used for the Kelvin units of temperature). At what temperature will the atoms energy level?

1-87 Calculate the average translational kinetic energy of an atom or molecule at 25℃ (298K).

1-88 Translational energy levels are so close together that they are considered to be continuous. Draw a diagram to represent translational energy levels for an atom or a molecule.

1-89 As the temperature increase, thermal energy is absobed by $J=4$ rotational levels of $^{1}H^{35}Cl$. to excite the atoms or molecules into higher translational energy levels. How much energy is regarded to excite an atom or a molecule from a given translational energy level to the next higher level?

1-90 As temperature increases, what should happen to the speed of rotation of a molecule?

1-91 As the molecule rotates faster, what happens to its rotational kinetic energy?

1-92 The rotational energy of a molecule is quantified. Using the energy model account for the increase in rotational kinetic energy when a molecule is heated.

1-93 How else might a molecule be excited to higher rotational energy levels?

1-94 The energy difference in rotational energy levels corresponds to light in the microwave region or electromagnetic radiation a molecule absorbs light with wavelength equal to 1.0 nm.

What is the difference in energy among the rotational energy levels which gives rise to this absorption?

1-95 Will there be any rotational energy at absolute zero?

1-96 Below is a typical rotational energy level diagram for a molecule. What does the arrow indicate? (Describe in term of what happens to the molecule.)

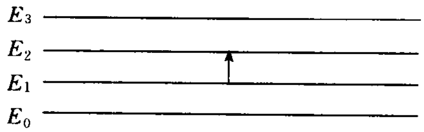

Figure 1-2

1-97 The first three rotational levels of the CO molecule have energies of 0, 7.6×10^{-23}J, and 22.9×10^{-23}J molecule. What is the wavelength of light necessary to excite the CO molecule from the E_1 to E_2 rotational level?

1-98 Figure 1-3 shows a portion of an atomic energy level diagram with the term symbol for each of the states represented shown at the right and the energy (in electron volts) of the shown at the left

(a) State the values of L, S, and J for each of the states.

(b) State the selection rules governing ΔL, ΔS, and J and show how they apply to transitions for the energy levels represented.

(c) Which of the allowed transitions will give rise to the lowest energy radiation?

Calculate the wavelength (in centimeters) of the emitted radiation.

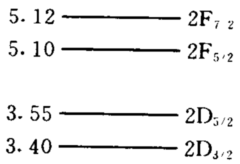

Figure 1-3

1-99 What are the values of L and J for a state with the term symbol ^{2}P?

1-100 How many lines are predicted by the selection rules for a $^3D_{3,2,1} \rightarrow {}^3P_{2,1,0}$ transition? Justify your answer by reference to the selection rules.

1-101 A portion of a term diagram for indium is shown in figure 1-4. Refer to this diagram as required to answer the following questions.

(a) List all the allowed transitions for the states shown.

(b) Pick the line or group of lines that is likely to have greatest emission intensity by flame atomic emission and justify your choice by reference to the expression describing the intensity of atomic (thermal) emission.

(c) If an external continuum source is used to observe the absorption of In atoms in flame, list the lines that will be seen in absorption.

(d) Write an expression describing the ratio of the absorption, (α_1 of the longest wavelength absorption line to the absorption, α_2 of the next shorter wavelength absorption line.

(e) If atoms in a flame are irradiated only with radiation of energy corresponding to the transition 5 $^2P_{\frac{1}{2}} \rightarrow {}^2S_{\frac{1}{2}}$ at what wavelengths, if any would your expect to see atomic fluorescence?

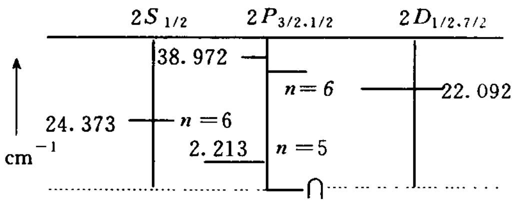

Figure 1-4 Partial term diagram for In

1-102 Figure 1-5 is a partial term diagram for Hg. Use the information provided on this diagram to answer the following questions.

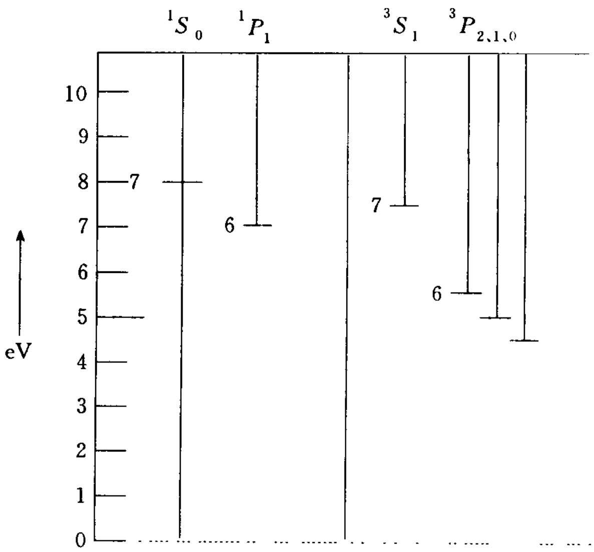

Figure 1-5 Partial term diagram for Hg

(a) Assuming that the selection rules are strictly obeyed, list the allowed transitions.

(b) Assuming that the selection rule governing ΔS is not operative, list any additional allowed transitions to the ground state.

(c) If an external continuum source is used observe the absorption of Hg atoms in a room-temperature vapor, list the transitions that will be seen if all the selection rules are obeyed.

1-103 If the $^3P_{2,1,0}$ states of Hg are thermally populated, calculate the ratio of the populations of $^3P_2$ and $^3P_0$ levels in a flame of 2 700K. The splitting is 6 398 cm^{-1} and $k = 0.697$ cm^{-1}/ K.

第二章　原子吸收光谱法

基本概念

2-1　对原子吸收分光光度分析做出重大贡献，解决了测量原子吸收的困难，建立了原子吸收光谱分析法的科学家是：

A. R. Bunren（本生）；　　B. W. H. Wollarten（伍朗斯顿）；

C. A. Walsh（华尔希）；　　D. G. Kirchhoff（克希荷夫）。

2-2　原子吸收光谱法是基于从光源辐射出待测元素的特征谱线的光，通过样品的蒸气时，被蒸气中待测元素的______所吸收，由辐射特征谱线光被减弱的程度，求出样品中待测元素的含量。

A. 原子；　B. 激发态原子；　C. 离子；

D. 分子；　E. 基态原子；　F. 电子。

2-3　原子吸收分析定量测定的基础是__________，但这是在假定______和__________的情况下进行的。

2-4　原子吸收光谱作为一种实用的分析方法是从 1955 年开始的，澳大利亚的华尔希（A. Walsh）发表了他的著名论文“__________”，奠定了原子吸收光谱分析法的基础。

2-5　在所有情况下，原子对辐射的吸收都是有选择性的，这种选择性是由原子的______所决定的。

2-6　使电子从基态跃迁到第一激发态所产生的吸收线，称为______。由于原子结构和外层电子排布不同，不同元素的原子从基态跃迁到第一激发态时所吸收的能量不同，所以这种吸收线又称为______。

2-7　原子吸收分光光度分析，是利用处于基态的待测原子蒸气，对从光源辐射的______的吸收来进行分析的。

2-8　在导出吸光度 A 与待测元素浓度 c 呈线性关系时，曾作过一些假定，以下哪一点是错误的？

A. 吸收线的宽度主要取决于多普勒变宽；

B. 通过吸收层的辐射强度在整个吸收光程内是恒定的；

C. 在 $\Delta\nu$ 频率范围内，吸收系数可近似地认为是常数；

D. 基态原子数 N_0 近似地等于原子数 N；

E. 在任何吸光度范围内都适合。

2-9　简述原子吸收光谱法的基本原理，写出定量分析的基本公式。为什么通常不用原子吸收光谱法进行元素定性分析？