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J. Edmund White

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PHYSICAL CHEMISTRY

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HBJ

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A B C D E

TEXTBOOK CORRELATION TABLE

The following table correlates the topics of this Outline with the pages of five major textbooks on physical chemistry. They were selected from two surveys conducted by the author to determine which textbooks were widely used.

These textbooks are listed below. The topics of this Outline and the pages on which they are covered are listed in the first two columns at the left of the table. The corresponding pages of each of the textbooks, designated by author, are listed in the next five columns. To find the pages of your textbook that correspond to the pages of this Outline, read across each row and down the column headed by your author's name.

Adamson, A TEXTBOOK OF PHYSICAL CHEMISTRY, 3rd ed., 1986, Academic Press

Alberty, PHYSICAL CHEMISTRY, 6th ed., 1983, Wiley

Atkins, PHYSICAL CHEMISTRY, 3rd ed., 1986, Freeman

Castellan, PHYSICAL CHEMISTRY, 3rd ed., 1983, Addison-Wesley

Noggle, PHYSICAL CHEMISTRY, 1985, Little, Brown

CHAPTER	THIS OUTLINE	ADAMSON	ALBERTY	ATKINS	CASTELLAN	NOGGLE
1: Preliminaries	1–17	24–25 91–92 187–188	ix 22–26 797–800 Front	49 59–62 Front	A1–A4 A17–A23 174–177 Back	899–900 909–913 Front
2: Gases	18–47	1–24 37–58	9–10 12–18 575–592	12–13 19–34 644–653	9–60 67–70 80	2–59 425–430
3. The First Law of Thermodynamics	48–77	105–129 146–147	19–22 26–29 31–36	38–54 57–75	93–94 96–129	68–110
4: Thermochemistry	78–95	155–169 172–174	36–45	79–92	129–144	111 250–257 795–796
5: The Second and Third Laws of Thermodynamics	96–116	183–204 210–215	54–76	96–108 113–116 121–122	94–95 153–174 177–189	118–137 145–152
6: Spontaneity, Equilibrium, and Free Energy	121–147	204–210 228–230 252–253 322–326	86–107 186–187	108–113 123–132 161–163	203–226 249–250	137–144 168–170 173–174 275–281 329–330
7: Chemical Equilibrium	148–176	239–255	175–185 187–192 197–199	213–224	5–6 229–244	262–274 281–292
8: Physical Equilibrium: A Single Substance	177–189	265–273 277–282	119–121 126–132	136–145 195–196	88 259–270	170–182 189–192

Continued on inside back cover

Continued from inside front cover

CHAPTER	THIS OUTLINE	ADAMSON	ALBERTY	ATKINS	CASTELLAN	NOGGLE
9: Physical Equilibrium: Liquid and Vapor Mixtures	190–228	311–322 335–341 359–369	132–144 149–151 154–155	164–181 200	277–285 287–309 311–313 323–324	317–329 334–339 345–352
10: Physical Equilibrium: Liquid and Solid Mixtures	229–245	341–343 393–409 417–420	121–123 151–154 155–158	174 192–202	271–274 285–287 319–337	310–314 352–357
11: Solutions of Electrolytes	246–278	370–372 431–474	217–221 723–728	234–245 663–674	354–369	364–378 381–395
12: Electrochemical Cells	279–305	499–524 528–529	211–217 221–228 229–231	245–254 259–274 278	371–395	395–416
13: Chemical Kinetics	306–336	541–584	602–628 630–631 634	687–705 714–716 724–725	799–861	466–475 480–510 526–530
14: Introduction to Quantum Theory	341–370	657–689	299–333	289–310 314–318	445–509	567–609
15: Quantum Theory of Atoms	371–396	689–707 716–721	334–369	341–362	511–530	641–665
16: Quantum Theory of Molecules	397–417	771–786 795–796	390–413 415	374–390	531–547 554–561	701–706 724–738 768–770 818–819
17: Symmetry and Spectroscopy	418–444	727–754 810–812 819–830	370–383 432–460	405–419 432–454	561–571 579–583 625–636 638–640 642 646	780–794 820–834 836–840
18: Statistical Mechanics	445–458	131–135 215–221 224–226	525–542	506–521 534–541	189–196 721–728 731	848–856
19: Solids and Surfaces	459–472	284–290 595–597 863–870 881–883	275–278 279–281 287–290 749–769	151–155 549–556 770–782	407–408 413–414 426–428 682–685 691–703	182–187 538–542

PREFACE

Do not read this Outline—use it. You can't learn chemistry of *any* variety simply by reading it: You have to *do* it, in the laboratory and on paper. Solving specific, practical problems is the best way to master—and to demonstrate your mastery of—the theories, laws, and definitions that make up physical chemistry. Outside the laboratory, you need three tools to do physical chemistry: a pencil, paper, and a calculator. Add a fourth tool, this Outline, and you're all set.

This HBJ College Outline has been designed as a tool to help you sharpen your problem-solving skills in physical chemistry, skills that are vital to success in a "p-chem" course. Although some of your examinations may contain a few questions involving explanations, derivations, or diagrams, most of the questions you'll be asked in your course will be problems to be solved. Your knowledge of concepts, terms, and laws will be measured by your success in applying them to the solution of problems.

Each chapter of this Outline covers a major topic, whose fundamental principles are broken down into outline form for easy reference. The text is heavily interspersed with worked-out examples, so you can see immediately how each new idea is applied in solving a problem. Each chapter also contains a Summary and a 'flowchart' of the major equations which, taken together, will enable you to review the primary principles of the chapter and the connections between the equations expressing those principles.

Most important, this Outline gives you plenty of problems for practice. Work the Solved Problems before you read the answers; then check yourself against the step-by-step solutions provided. Show your mastery of the material in each chapter by doing the Supplementary Exercises. (In the Supplementary Exercises, you're given answers only—the details of the solution are up to you.) Finally, test yourself on the topics covered in the Outline by taking the two Mid-Semester Exams and the two Final Exams. The solutions to all exam questions are given in detail, so you can use them to diagnose your own strengths and weaknesses.

Remember that this is an *outline,* to be used as a complement to your textbook or for review. This Outline *does not* contain every topic found in a typical physical chemistry textbook, but it does contain the fundamental topics common to all textbooks. Be sure you understand these fundamentals before you try to learn the more advanced aspects of the topics that are included in your course. To relate this Outline to your textbook, use the Textbook Correlation Table, which correlates chapters of the Outline with pages in several of the leading textbooks of physical chemistry.

The choice of topics to include—and the emphasis to give each—was based partly on a report of a committee of the Division of Chemical Education of the American Chemical Society (ACS) and partly on analysis of examinations shared with me by seventeen other professors. Statistical mechanics, for example, was treated lightly in these materials, so Chapter 18 is quite brief. I have omitted or merely introduced some advanced topics that have "trickled down" into the beginning physical chemistry textbooks, but I have included some topics that seem to have "trickled out." I believe that the latter could be helpful to many students whose difficulties with a p-chem course or textbook may be due to lack of familiarity with basic concepts.

You may find differences between the symbols used in this Outline and those used in your textbook. Probably no two books are exactly alike in this regard; each author must make his/her own choices for symbols—and for units as well. The SI system of units, which I have used extensively, now bears official approval, but other systems still exist. So I have mixed in other units that have been used regularly in the past because they still turn up in older tables, books, and (especially) journals. At first, you may be confused by the variety of symbols and units; but, as you work with these symbols and units, converting them from one to another, they will become familiar, and you will be prepared for almost any situation.

I wish to acknowledge support from Southern Illinois University at Edwardsville: I wrote most of the first draft while I was on sabbatical leave, the Office of Research and Projects provided some help on typing, and the Department of Chemistry provided some supplies, copying, and assigned time. Colleagues Thomas Bouman and David Rands helped on some of the physical chemistry, and Antony Wilbraham was supportive and helpful from his experience as a successful textbook author. Special thanks are due to Dr. Gordon R. Franke of Northeast Missouri State University, who read every word of the manuscript, caught errors, and offered many valuable suggestions which greatly improved both text and problems. My HBJ editors, Charles Arthur and Philip Unitt, also made useful suggestions and caught errors. Any remaining errors are, of course, the responsibility of the author. Finally, I thank my wife, Betty Evans White, for her encouragement to undertake the project, for her constant support, and for her patient acceptance of various deprivations during the long process of completing it.

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CONTENTS

1 PRELIMINARIES

THIS CHAPTER IS ABOUT

☑ **Dimensions, Units, and SI**
☑ **Constants and Conversion Factors**
☑ **Essentials of Logarithms**
☑ **Essentials of Calculus**

1-1. Dimensions, Units, and SI

A. Dimension and unit

The terms *dimension* and *unit* have different meanings and can't be used interchangeably. A **dimension** is a concept or abstraction that expresses a type of measurement, e.g., length or time. A **unit** is a specific amount of a dimension that serves as a reference for actual measurement, e.g., meters or seconds. **Dimensional analysis** is a mathematical approach for analyzing the dimensions involved in a problem and its answer without regard to numerical values or units.

EXAMPLE 1-1: For a problem that requires division of an area by a volume, show that the answer will contain the dimension of length (actually, the reciprocal).

Solution: Since area and volume both contain the dimension of length (one squared and the other cubed), we write

$$\frac{(\text{Length})^2}{(\text{Length})^3} = \frac{l^2}{l^3} = l^{-1}$$

Note that we did not use any units.

EXAMPLE 1-2: List some commonly used units of the dimension *length.*

Solution: Inch, foot, mile, furlong, rod, meter, and kilometer.

B. Physical quantities

A number by itself has no physical meaning; it is dimensionless. If a number is followed by a unit, the combination is a measurement of a **physical quantity**.

EXAMPLE 1-3: The number 6.022×10^{23} by itself has no meaning, although you will recognize it as the number of objects represented by Avogadro's number, N_A. When a unit is added, it becomes Avogadro's constant, $L_A = 6.022 \times 10^{23}$ [objects] mol^{-1}. This constant contains the dimension *amount of substance.*

C. International system of units

By international agreement, seven dimensionally independent physical quantities have been selected as the foundation of a system of units, known as SI from the French *Le Système*

TABLE 1-1: Defined and Derived SI Units

Base Quantities and Units

Physical quantity	Symbol	Unit	Symbol
Length	l	meter	m
Mass	m	kilogram	kg
Amount of substance	n	mole	mol
Thermodynamic temperature	T	kelvin	K
Time	t	second	s
Electric currrent	I	ampere	A
Luminous intensity	I_v	candela	cd

Quantities with Derived Units

Physical quantity	Unit	Symbol	Definition in base units
Force	newton	N	kg m s^{-2}
Pressure	pascal	Pa	$\text{kg m}^{-1}\text{ s}^{-2}$
Energy	joule	J	$\text{kg m}^2\text{ s}^{-2}$

International d'Unités. A **base unit** has been designated for each quantity. These seven quantities are listed in Table 1-1 along with their base units and symbols.

note: The **amount of substance** is a new concept of physical quantity, and the meaning of its symbol conflicts with prior usage. The symbol is n, and it requires *both a number and a unit*. The unit is the **mole**. Thus it is not correct to say "n moles"; rather, "$n = y$ moles," where y is the number of moles.

EXAMPLE 1-4: Consider an analogy between length and amount of substance. Length is designated by l, and let's say that we have $l = 5$ m. The l is not just the number of meters, "5," or the unit, "meters"; the l is the whole expression, "5 meters." Thus for an amount of substance, n, we might have $n = 5$ mol. Both the number and the unit are required to describe n completely.

EXAMPLE 1-5: If we have 64 grams of sulfur, we could say that we have 2 moles of sulfur, but how would we write it?

Solution: We should not write "$n = 2$." The correct use of n is "$n = 2$ mol," a number and a unit. Since the substance is known, "2 mol S" is even better.

D. Numerical values of physical quantities

We obtain the numerical value of a quantity by dividing the quantity by the unit.

EXAMPLE 1-6: For 2 moles of sulfur, we would write

$$\text{Number of moles} = \frac{n}{\text{mol}} = \frac{2\text{ mol S}}{\text{mol S}} = 2$$

We emphasize the distinction between a quantity and its numerical value because it is important in certain situations.

EXAMPLE 1-7: A table of thermodynamic data has a column headed $\Delta H_v/\text{kJ mol}^{-1}$. **(a)** Why is this designation used? **(b)** How should we read the table?

Solution:

(a) The table contains a list of numbers, not physical quantities. Let's use a physical quantity of

$\Delta H_v = 41$ kJ mol^{-1}. Its numerical value, as illustrated in Example 1-6, is

$$\text{Numerical value} = \frac{\Delta H_v}{\text{kJ mol}^{-1}} = \frac{41 \text{ kJ mol}^{-1}}{\text{kJ mol}^{-1}} = 41 \tag{1-1}$$

The column heading tells us that the physical quantity was divided by its units and the numerical value was entered in the table.

(b) To read the table (i.e., to find a ΔH_v), we simply find the number for a particular compound and write the units after it: 41 kJ mol^{-1}. More precisely, we are applying Eq. (1-1):

$$41 = \frac{\Delta H_v}{\text{kJ mol}^{-1}}$$

Cross-multiplying gives $\quad \Delta H_v = 41 \text{ kJ mol}^{-1}$

E. Derived quantities and units

Other physical quantities are derived from the seven SI base quantities. Their units are expressed as combinations of the defined (base) units. Some of the derived units (e.g., the pascal) were named for famous scientists. A few of the derived quantities and units are included in Table 1-1.

EXAMPLE 1-8: The dimensions of velocity are length and time (reciprocal), or, in symbols, $l \times t^{-1}$. The base units of length and time are meters and seconds, respectively. Thus the derived unit for velocity is, in symbols, m s^{-1}.

EXAMPLE 1-9: Newton's first law is Force = Mass × acceleration. (**a**) What are the dimensions of force? (**b**) What are the units of force?

Solution:

(**a**) The dimensions of acceleration are $l \times t^{-2}$; thus force equals $m \times l \times t^{-2}$.

(**b**) The base units of m, l, and t are kg, m, and s, respectively, so the unit of force is kg m s^{-2}; this unit is called the *newton*, N. (See Table 1-1.)

F. Auxiliary units

An auxiliary unit is a combination of a prefix and a base unit. Prefixes are expressed in multiples or submultiples of one thousand. You are already familiar with milli- and kilo- for 10^{-3} and 10^3, respectively. The newer prefixes such as femto- for 10^{-15} seldom appear in physical chemistry. Strictly speaking, the quantity 10 cm should be written as 10^{-1} m or 10^2 mm, but the well-established prefixes centi-, deci-, and deca- are still allowed by SI rules.

1-2. Constants and Conversion Factors

A. Precision of constants

The numerical values of fundamental physical constants are usually known to six or seven significant figures. This degree of precision is far greater than the experimental error in most undergraduate experiments and isn't needed for solving most practice problems. We usually round off constants to four significant figures; but, for practice problems, we may further shorten the values to three significant figures. Some examples of frequently used constants are given in Table 1-2.

TABLE 1-2: Some Fundamental Constants

Avogadro constant	L_A	$6.022\,05 \times 10^{23}$ mol^{-1}	Planck constant	h	$6.626\,18 \times 10^{-34}$ J s
Boltzmann constant	k	$1.380\,66 \times 10^{-23}$ J K^{-1}	Electron charge	e	$1.602\,19 \times 10^{-19}$ C
Faraday constant	$\mathcal{F}$	$9.648\,46 \times 10^4$ C mol^{-1}	Electron mass	m_e	$9.109\,53 \times 10^{-31}$ kg
Gas constant	R	$8.314\,41$ J K^{-1}mol^{-1}	Speed of light	c	$2.997\,93 \times 10^8$ m s^{-1}

B. Conversions

The data for solving a problem may not be compatible with each other or with the available constants, making conversions necessary. In your general chemistry course, you learned to include the units when you set up a calculation and then to make sure that you canceled or multiplied them properly to end up with the correct units for the answer. This is even more important in physical chemistry because the problems are more complex. Verifying units is a good way to check your work.

1. The simplest conversion is the addition of a constant.

EXAMPLE 1-10: Convert 30.00 °C to the Kelvin scale.

Solution: One degree on the Celsius scale is equal to one degree on the Kelvin scale, so we convert from Celsius to Kelvin by adding 273.15, the number of degrees between absolute zero and the freezing point of water. Recalling the point made in Example 1-7 with Eq. (1-1), we should write

$$\frac{T_K}{\mathrm{K}} = \frac{T_C}{^\circ\mathrm{C}} + 273.15$$

If $T_C = 30.00\ ^\circ\mathrm{C}$,

$$\frac{T_K}{\mathrm{K}} = \frac{30.00\ ^\circ\mathrm{C}}{^\circ\mathrm{C}} + 273.15 = 303.15 \qquad \text{or} \qquad T_K = 303.15\ \mathrm{K}$$

---

2. Most conversions require multiplication by a conversion factor.

EXAMPLE 1-11: To convert mm to m, we need the relationship 10^3 mm = 1 m. You could probably work out in your head that 50 mm = 5×10^{-2} m, but how would you write a mathematical equation to get this answer?

Solution:

$$(50\ \mathrm{mm})\left(\frac{1\ \mathrm{m}}{10^3\ \mathrm{mm}}\right) = 50 \times 10^{-3}\ \mathrm{m} = 5.0 \times 10^{-2}\ \mathrm{m}$$

Note in Example 1-11 that (1 m)/(10^3 mm) = 1. *A conversion factor is unity.* Multiplying by 1 does not change a quantity, but it does change the units in which the quantity is measured.

C. Non-SI units

The use of certain well-established units (e.g., liter, atmosphere, calorie, and angstrom) may eventually end. Until then, you will continue to encounter them in tables, books, and articles; you will need to know how to convert them to SI units. Several of these conversion factors are

1 atmosphere = $1.013\,25 \times 10^5$ Pa
1 liter = $10^{-3}\ \mathrm{m}^3 = 1\ \mathrm{dm}^3$
1 bar = 10^5 Pa
1 calorie = 4.184 J

EXAMPLE 1-12: A new table of thermodynamic properties from the National Bureau of Standards uses 1 bar as the standard-state pressure. (The *bar* is not an SI unit but is a simple multiple of one, the pascal.) Find the value of the pressure–volume gas constant, $R = 0.082\,05$ L atm $\mathrm{K}^{-1}\mathrm{mol}^{-1}$, for this new pressure unit.

Solution: You know that

1 atm = $1.013\,25 \times 10^5$ Pa
1 Pa = 10^{-5} bar
1 atm = 1.013 25 bar

So $$R = 0.082\,05\,\frac{\text{L atm}}{\text{K mol}}\left(\frac{1.013\,25\text{ bar}}{1\text{ atm}}\right) = 0.083\,14\,\frac{\text{L bar}}{\text{K mol}}$$

Note that the conversion from atmospheres to bars causes a change of about 1.3% in the numerical value, which is close to experimental error in many cases. For practice problems, we will use atmosphere or bar interchangeably, as if they were identical. For a real situation involving three or four significant figures, you should convert atmospheres to bars.

1-3. Essentials of Logarithms

A. Exponential nature

The **logarithm** of a number to a certain base is the power to which that base must be raised to give the number. If a is the base,

$$u = a^{\log u} = a^{v} \tag{1-2}$$

where $v = \log_a u$.

The usual bases are 10 and e ($e = 2.718\,28\ldots$). The abbreviation log is used routinely to represent logarithms to the base 10, and ln is used for logarithms to the base e. Thus the symbol $\ln x$ may be read "the *natural* logarithm of x to the base e." The relationship between the two systems of logarithms is

$$\ln u = 2.303 \log u$$

which may be expressed as a conversion factor:

$$\frac{\ln u}{2.303 \log u} = 1$$

The exponential character of logarithms makes them useful for expressing exponential relationships between physical quantities. In general, if the dependence of one quantity on a second quantity is proportional to the value of the second quantity, the dependence is exponential. Specific cases include distribution functions, first-order reactions, and the barometric formula. Treating such cases mathematically usually requires calculus and the expression $du/u = \ln u$.

EXAMPLE 1-13: The dependence of u on v is proportional to u. Express this as an exponential and as a logarithm.

Solution: The dependence can be written as

$$\frac{du}{dv} = ku$$

where k is a proportionality constant. Rearranging gives

$$\frac{du}{u} = k\,dv$$

We now have to use calculus. Letting $u = u_0$ when $v = 0$, we integrate between the limits u and u_0 and v and 0:

$$\int_{u_0}^{u} d\ln u = k\int_{0}^{v} dv$$

$$\ln\frac{u}{u_0} = kv$$

$$\frac{u}{u_0} = e^{kv}$$