

# Chapter 1

## Quantitative Problem Solving in Physical Chemistry

**Abstract** This introductory chapter develops and discusses a concept of mathematically oriented problem-solving in physical chemistry. Based on a definition of the scientific discipline physical chemistry, the basic skills needed for successful problem-solving are identified. The concept of problem-solving is exemplified using a sample problem text. Finally, an overview of the problems in the various chapters is given, along with comments on the level of difficulty and thematic cross-links among the various topics.

### 1.1 A Concept for Problem-Solving in Physical Chemistry

Physical chemistry is a scientific discipline that explores chemical topics using physical theory and technique. This definition also explains the rather challenging nature of the subject physical chemistry taught as part of university curricula. It combines three basic skills that we must develop in the course of our studies. First, we should have enough of a chemical background to understand the problem. Second, we must know the fundamental laws of physics and we need to develop some sense of the significance of fundamental physical quantities in chemical contexts.<sup>1</sup> Third, we must be able to apply basic mathematical methods to work out quantitative results.<sup>2</sup> Finally, *experience* including the ability of *recognition* is a fourth necessary ingredient that considerably enhances our effectivity in problem-solving. This is quite a lot. For the solution of a concrete, non-trivial problem of a certain complexity, all these skills need to be combined to work out a solution.

In this introductory chapter, a short guide to dealing with physical chemistry problems is offered to cultivate your problem-solving skills. It picks up on the typical difficulties experienced by students that I have noticed over a period of

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<sup>1</sup>An example of such a fundamental physical quantity is *energy*. Indeed, it is worth reflecting on the significance of energy in conjunction with nearly all key topics, ranging from changes of state (Chap. 3) to quantum mechanics and spectroscopy (Chaps. 9 and 10).

<sup>2</sup>In fact, mathematics has been called the *language of physics* [1]. A mathematical formulation of a problem combines exactness with the complete refinement to the essential facts in a quantitative manner.

teaching of about 15 years at a faculty of engineering.<sup>3</sup> The scheme assumes a problem of relatively high complexity that requires both logical linking of facts from one or more contexts, along with the setup and execution of a mathematical solution. The five different stages listed do not follow a strictly sequential scheme. Instead, these stages are merely simultaneous intellectual activities that work together to find the solution.

**1. Read the problem text carefully.**

- (a) Which quantities are given?
- (b) What is going to be calculated?
- (c) Analyze the problem text with regard to special key words.

**2. Use your experience to identify the essential issues.**

- (a) Relate the problem to a topic in physical chemistry.
- (b) Identify matches with contents from lectures, seminars, and laboratories.
- (c) Make a sketch that collects and illustrates the important facts.
- (d) Narrow the problem down as far as possible to identify the essential issues that are inevitable for the solution of the problem.

**3. Assess the points you do not yet understand.**

- (a) Think pragmatically! Distinguish those details you consider crucial from those that are merely decorative.
- (b) If crucial details are lacking, reflect again on the essential issues that might be missing.
- (c) If you think that essential quantities are undefined in the problem text, will these quantities be cancelled out at the stage of the mathematical solution?
- (d) Based on your experience, reflect on the expected results.
- (e) Be critical: are you convinced that you have found the correct approach?

**4. Work out the solution—translate the problem into the language of mathematics**

- (a) Write down the key equations on the basis of the essential issues identified.
- (b) Reflect on potential technical difficulties, e.g., those related to undefined quantities (see above).

**5. Accomplish the solution**

- (a) Think pragmatically! Possible technical difficulties may be resolved by the solution.
- (b) If you have obtained results, assess their plausibility.
- (c) Reflect again on the solution. Are you convinced that you have found the correct solution?

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<sup>3</sup>An extensive analysis of such difficulties can be found in [2].

As an example of a concrete problem text, consider Problem 3.13 on page 64. The problem text is reproduced here and the quantities provided and sought, along with the key-words according to points 1.a, 1.b, and 1.c, are highlighted:

At 293 K, the vapor pressure of the solvent diethyl ether ( $\text{C}_2\text{H}_5\text{-O-C}_2\text{H}_5$ ) is 586 hPa. After the addition of 20 g of an unknown non-volatile compound in 1 kg diethyl ether, the vapor pressure reduces to 583 hPa. Assume an ideal mixture of diethyl ether and the unknown compound, for which an elementary analysis yields mass fractions of 41.4% carbon, 5.5% hydrogen, 9.6% nitrogen, and 43.8% oxygen. Determine the molar mass and the molecular formula of the unknown compound.

Let us look at the various stages of this problem-solving scheme. Careful reading of the text is important. We must analyze the problem with regard to the quantities given and the quantities to be calculated. In preparation for stage 4, we should assign a unique symbol to each quantity. Note that in many cases it is crucial to distinguish between the initial value of a certain quantity and its value in the final state, or the values that the quantity takes during an ongoing process. In the concrete problem, we must distinguish between the vapor pressure of *pure* diethyl ether (a common symbol would be  $p^*$ ), and its vapor pressure in the binary mixture (symbol  $p$ ). Moreover, it is crucial to define all quantities in the same system of units, usually the SI system. Sometimes you need to convert some of the quantities (see Table A.2 in the appendix).

In the second stage, the *essential issues*, which are inevitable for the solution of the problem, are identified. A first assignment of the problem to a general topic is made based on the recognition of lecture content, seminar work, laboratory work, etc. Quite often, we find such essential issues coded in *key words* appearing in the problem text. In the concrete problem, such a key-word is the ideal mixture, implying the application of Raoult's law (Eq. (3.108) on page 54). Another essential issue is stoichiometry and the definition of the mole fraction and molar mass. A third ingredient is the fact that the solvent diethyl ether and the unknown compound constitute a *binary mixture*—a point that is not explicitly stated in the problem text. Sometimes, it is quite useful to make a sketch to collect and arrange such essential issues visually, and to identify the logical links between them. This is especially true for problems involving processes with an initial state and a final state.

Depending on your experience and the complexity of the problem, you will not immediately identify the correct approach. In this case, it is important to assess the points you do not yet understand (stage 3). Sometimes, it is good advice to think pragmatically. For example, do not become intimidated by problem texts filled with impressively long names of chemical compounds. Sometimes, you just need the

molecular formula to determine a molar mass; in other cases, they can be replaced altogether by shorter symbols. At the stage where you do not yet see through the solution pathway, a detail that is lacking, such as an undefined quantity may be canceled out in the calculation. However, it may also indicate that you have missed something. Be hopeful and at the same time critical with the setup of your solution.

The next step is to write down the equations resulting from the list of essential issues identified (stage 4). The more experience we have, the easier it is to transpose the solution concept into a set of mathematical equations. In fact, at a level of deeper understanding, the student's conceptual view based on essential issues and the mathematical formulation tend to merge. Also at this stage, we must be critical: the appearance of undefined quantities in the equations, but also too many redundant quantities, could indicate flaws in the approach and may force a reassessment. At the last stage, where the solution has been found, you should check the plausibility of your results. It is worth comparing the results with the initial estimations. An approximate agreement within the same order of magnitude strengthens the confidence with regard to the method of solution. Large differences, in contrast, require critical reflection on the entire method of solution. In this case, it is a good idea to consider possible technical errors first, e.g., arithmetic errors, such as confusion of signs or the addition of quantities with different physical units. Unexpected deviations in spite of a correct solution, in contrast, invite us to rethink a topic from a new perspective. In fact, in this case, a problem can prove to be highly useful to the individual student.

Note that not all problems collected in this book fit exactly into the scheme proposed above. For example, there are numerous problems where we prove a certain relationship before it is applied to a concrete case. Another popular category of problems involves a graphical solution or, in some cases, a numerical treatment using a computer.

## 1.2 Overview of Problems

In the following, the problems presented in the various chapters are listed.

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The order of topics in this workbook roughly follows the way in which physical chemistry is presented in contemporary textbooks. Stoichiometry (Chap. 2) is the natural starting point of any quantitative treatment in general chemistry. Moreover, stoichiometry is a prerequisite for the understanding of fields such as chemical equilibrium (Chap. 5) and chemical kinetics (Chap. 6). The attentive reader will notice that certain concepts such as the extent of reaction introduced in Chap. 2, are systematically used in the subsequent chapters.<sup>4</sup> In this sense, the arrangement of problems has an intrinsic order. But this should by no means prevent the reader from entering into the problems at an arbitrary point. In a few cases where the solution of a problem assumes that the reader has dealt with the preliminary contents of other problems, this is explicitly noted.

Concerning the complexity of the problems, the level of difficulty gradually increases from chapter to chapter, not only from a mathematical, but also from a conceptual point of view. Concerning mathematics and the methods of solution, the attentive reader will notice interesting parallels. A prime example is the set of problems dealing with *oscillating chemical reactions* (Problems 6.6 and 6.7) in the chapter on reaction kinetics on the one hand, and the set of problems dealing with *LASER* operation in Chap. 10 (spectroscopy) on the other.<sup>5</sup> Seemingly an accidental mathematical conformity at first sight, these similarities reveal a *hidden* relationship with regard to interaction in complex systems that the reader might discover.<sup>6</sup>

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<sup>4</sup>In my experience, many students are reserved in using the extent of reaction in concrete problems. Not appearing explicitly in any fundamental laws such as the law of mass action, it seems somehow dispensable. In fact, it is possible to work out a correct solution without using it explicitly. However, this requires an intellectual effort that unconsciously achieves the same purpose as the conscious use of this concept would do systematically.

<sup>5</sup>In fact, for the numerical solution of the laser equations in Problem 10.11, you can use the computer code of Problem 6.7, with only small modifications.

<sup>6</sup>The present book can, of course, only draw the reader's attention to such points without analyzing the relationships in full detail, as has been done by Hermann Haken [3].

In Chap. 9 dealing with quantum mechanics, problems highlighting some rather abstract aspects of quantum mechanics, such as operator algebra, were included, for several reasons. First, the interpretation of quantum mechanics raises interesting discussions in seminars. Second, operator algebra in quantum mechanics is a powerful method of producing results with sometimes surprisingly sparse efforts.<sup>7</sup> Third, graduate students starting to listen to specialized conference talks, e.g., in spectroscopy, will experience the necessity of being familiar with these methods for their future scientific work.

## References

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3. Haken H (2004) *Synergetics*. Springer, Heidelberg

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<sup>7</sup>An instructive example is the solution of the quantum double well problem (Problem 9.17) for which the energy levels can be calculated with arbitrary precision without solving one single integral explicitly.