

Introductory chemical dynamics: using the chemical potential from the start

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Sumario. Los procesos químicos –aquellos asociados con el transporte, variación y reacciones en las sustancias- dan paso a un rico mundo de fenómenos, interesante tanto para los físicos como para los químicos y biólogos. Históricamente, la abundancia de fenómenos ha conducido a una amplia gama de maneras de describirlos. Mayormente a través del trabajo de Georg Job, recientemente ha quedado claro que la descripción se puede unificar si el potencial químico se presenta con una relevancia adecuada en los modelos de los cambios químicos. Para utilizar la fuerza del potencial químico para describir los fenómenos, el concepto debe introducirse desde el principio en cualquier curso de química o química física. Es igualmente importante motivar su construcción de manera intuitiva y no crear una cantidad derivada laboriosamente de otras aparentemente más básicas. En este artículo se presentan y discuten un número de fenómenos cuya descripción sugiere la existencia de un concepto unificador de fuerza motriz química. Utilizando el razonamiento analógico, es decir, comparando descripciones de procesos químicos y teorías de fluidos, electricidad o calor, vemos que la fuerza motriz puede ser concebida como la diferencia de los potenciales químicos de las especies involucradas en el transporte o las reacciones. Se demuestra como la noción de potencial químico y su diferencia puede conducir a modelos bastante simples, pero poderosos, del cambio químico.

Abstract. Chemical processes -those associated with the transport, change, and reaction of substances- open up a rich world of phenomena which is just as interesting for physics as it is for chemistry or biology. Historically, the wealth of phenomena has led to a plethora of forms of description. Largely through the work of Georg Job, it has become clear in recent years that descriptions can be unified if the chemical potential is given its proper relevance in models of chemical change. To make use of the power of the chemical potential in describing chemical phenomena, the concept should be introduced from the beginning in any course of chemistry or chemical physics. It is equally important to motivate this construct intuitively and not make it a quantity derived laboriously from other seemingly more basic ones. In this paper, we present and discuss a number of phenomena whose description suggests the existence of a unifying concept of chemical driving force. Using analogical reasoning, i.e., by comparing descriptions of chemical processes to theories of fluids, electricity, or heat, we see that the driving force can be conceived of as the difference of the chemical potential of the species involved in transports or reactions. It will be demonstrated how the idea of the chemical potential and its difference can lead to rather simple yet powerful models of chemical change.

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1 Introduction

The chemical potential is commonly treated as a complex derived quantity and, as such, is assumed to be hard

to grasp. When it is introduced, it is derived in terms of concepts from thermodynamics. Therefore, we do not commonly view the chemical potential as a quantity in its own right that can be introduced as a primitive con-

cept (i.e., not derived in terms of others).

It will be shown that we can create courses for high school or university level that make use of the chemical potential right from the beginning. We would like to demonstrate how this concept can be introduced in a simple way. The power of the concept of chemical potential should become apparent if we learn to produce useful models of chemical processes by directly using this fundamental quantity rather than relying on indirect arguments.

The approach discussed here has been developed largely by G. Job¹⁻⁶, and has been adapted for high school by F. Herrmann.^{7,8} It has been used in the context of a dynamical theory of heat by H. Fuchs⁹. Lately it has been demonstrated that the chemical potential can be fruitfully applied in simple dynamical modeling of chemical processes¹⁰.

(Refs. 2, 3 available at http://www.physikdidaktik.uni-karlsruhe.de/publication/konzepte/4_jobb.pdf and the same with 2_job). Ref.7, English translation: http://www.physikdidaktik.uni-karlsruhe.de/publication/pub_fremdsprachen/englisch.html. Partial Spanish translation: http://www.physikdidaktik.uni-karlsruhe.de/publication/pub_fremdsprachen/spanisch.html).

2 Phenomena involving the transport and change of substances

Here is a small list of chemical processes from the huge variety found in nature and in technical processes. They seem so different that a unified description appears to defy human imagination. Perhaps for this reason we find different conceptualizations for virtually every type of process having to do with chemical substances. However, it turns out that we need only a very small number of concepts to understand different phenomena.

Bread dries when left lying around. Water left in a puddle after a rainstorm evaporates. CO₂ can be dissolved in water in quantities that depend upon circumstances. Salt water freezes at a lower temperature than fresh water. A red blood cell ruptures when placed in fresh water. Iodine dissolved in water moves into ether if the latter is mixed into the water-iodine mixture. The polarization of light passing through a solution of glucose in water changes slowly in the course of time and finally reaches a stable value. Radioactive substances decay. Medication becomes ineffective if stored for too long. Baking soda added to an aqueous solution of citric acid lets the solution foam up violently, and the mixture becomes rather cold.

In the following, four processes will be described in more detail, and word models will be given. The explanations suggest that we can conceptualize very different processes economically by introducing a single concept, namely the *chemical potential*. The difference of the

chemical potential (of a species in different states or locations, or between different species) is considered the *driving force* of chemical processes.

Diffusion. Consider the concentration of salt dissolved in water. If there is a body of water at rest, and a small amount of salt is dissolved in only the bottom layer, the upper layers slowly receive salt as well whereas the concentration in the lower layer(s) decreases (Figure 1). It turns out that the concentration becomes homogenous in the end: the process—called *diffusion*—stops when the concentration of salt is the same everywhere.

Figure 1. Concentration of salt in adjacent layers of water in the course of time. The change of concentration is said to be the result of diffusion.

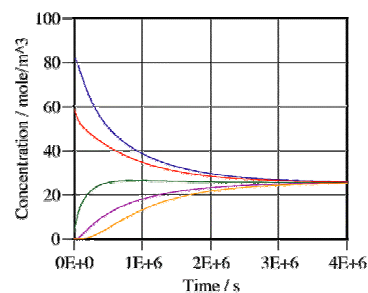
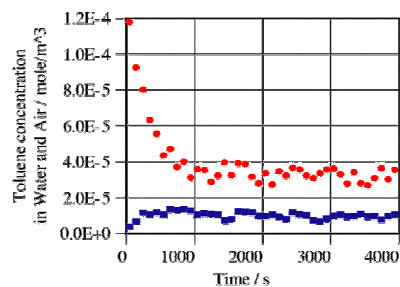


Figure 2. Concentrations of toluene in water and air measured as functions of time. Upper curve: water. Data courtesy J. Hosang.



There are similar phenomena in electricity, heat, and motion. The explanations of all these phenomena involve a single type of concept. We imagine an *intensive* quantity for electric, thermal, or mechanical processes which we call a *potential* (electric potential, temperature, angular speed). Differences of these potentials are conceptualized as *driving forces* for their respective processes. The processes involve the flow (and/or production) of *fluidlike* quantities—electric charge in electricity, entropy in thermal phenomena, and angular momentum in rotation.^{9,11}

This form of explanation that makes use of a strong form of analogical reasoning can be transferred to the case of diffusion of substances. There is a *chemical potential* associated with salt dissolved in water (which depends upon the concentration of salt). Smaller concentration means lower chemical potential. Salt flows through water as long as there is a difference of its chemical potential in different parts of the container.

Toluene in the environment. The previous example might suggest that we do not need a new concept such as the chemical potential; concentration suffices for an explanation. However, the following observation shows that we need a generalized intensive quantity to understand chemical processes. Toluene diffuses from water

into air (or vice-versa) until its concentration is about four times higher in water than in air (Figure 2).

The dynamic behavior seen in Figure 2 is basically the same as in the examples described so far, suggesting an explanation of similar type. However, it appears that toluene “prefers” to be in water rather than in air. So, if there are equal concentrations of toluene in water and air in contact, there still is a drive of toluene to migrate into water. Again, we can explain this by introducing the concept of chemical potential. At equal concentrations, the chemical potential of toluene is lower in water than in air. The difference of the chemical potentials of toluene in water and in air is interpreted as the drive (or driving force) for the diffusion of toluene. The observation tells us that the driving force for the flow of toluene cannot be differences in its concentration; rather, it is a gradient of the chemical potential of a substance.

Mutarotation of glucose. Glucose exists in two different configurations (called anomers) that only differ in the spatial arrangement of the elements in its molecules. The configurations are called α -glucose and β -glucose, respectively. At first, we only have α -glucose. If we dissolve it in water, part of it will change slowly into β -glucose. This is seen if we measure the angle by which light is rotated as it passes through an aqueous solution of glucose. The angle changes in the course of time, and this indicates changing concentrations of the anomers (Figure 3).

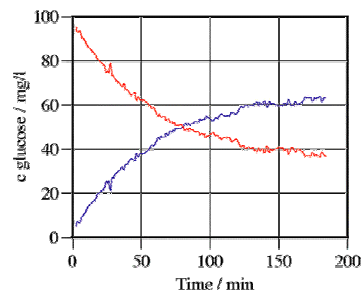
This is interpreted as follows: A configuration of glucose has a tendency or drive to change or decay, i.e., there is a tendency for a chemical reaction. The strength of this tendency can be expressed in terms of the chemical potential, just as shown in the case of the tendency of a substance to disperse. α -glucose and β -glucose have different chemical potentials, and these potentials also depend upon concentration. Once the chemical potentials have become equal, the reaction stops. The experiment shows that the chemical potentials of α -glucose and β -glucose become equal at different concentrations.

Decay and elimination of a radioactive substance. Radioactive substances are sometimes used in performing medical tests. Their presence and their concentration may be measured by the activity they produce (Figure 4). The substance decays and is excreted at the same time which means that the processes run in parallel.

Both processes are chemical in nature, the former is a transformation (reaction) whereas the latter is a form of transport. Either one of the processes can be understood as being governed by the chemical potential of the species. Here, the chemical potential depends upon the nuclear state, the concentration, and the biological environment. There is a tendency of the substance to decay, and there is a tendency to migrate. Nuclear reactions lead to the typical exponential decay, whereas elimination from the body can be modeled as being dependent on the difference of concentrations (as in diffusion) which, in the simplest case, also leads to exponential

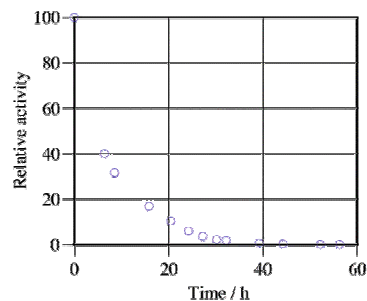
change.

Figure 3. Concentration of the anomers α -glucose (decreasing curve) and β -glucose in water as functions of time. α -glucose decays into β -glucose.



The concentration is determined by measuring the rotation of the plane of polarization of plane-polarized light shining through a solution of glucose. Data courtesy B. Sonnleitner.

Figure 4. Activity of Tc99m in a human body as a function of time.¹²



3 Intuitive conceptualization

An important part of the conceptualization of chemical processes is contained in the word models presented above. These models make use of the concept of chemical potential. Here we would like to show how the chemical potential relates to two more fundamental quantities: amount of substance, and energy.

Driving force, conversion rate, and power. The following discussion of chemical change is quite intuitive; it makes use of common sense reasoning. A chemical process consists of the flow and/or production (and destruction) of substances. The reason for such a process is found in a chemical driving force. When a chemical process runs by itself, it can cause other changes.

Note that there are three aspects of chemical change being used in this common sense explanation.¹³ (<https://home.zhaw.ch/~fusa/LITERATURE/Literature.html>).

There is a measure of *amount*, a measure of *tension*, and a measure of *power*. The first is formalized by introducing the amount of substance (which is the extensive thermal quantity), the second is cast in the form of the difference of the intensive chemical quantity (the chemical potential), and the third (causation) is measured in terms of energy or power.

There is a simple relation between these three basic concepts. The faster the chemical conversion (the higher the conversion rate), the higher the chemical power. Furthermore, the higher the driving force of a conversion for given conversion rate, the higher is the power. If we

express the conversion rate by the symbol I_n , and the driving force by $[\Delta\mu]_R$, the power of the process is⁹

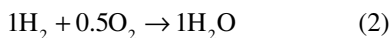
$$P_{chem} = [\Delta\mu]_R I_n \quad (1)$$

This relation can be interpreted graphically with the help of process diagrams. Figure 5 shows such a diagram for a battery—a device where a spontaneous chemical reaction drives an electric process.

4 Driving force of a reaction

In this section, we will discuss how we can deal with interesting everyday processes on a rather simple level if we have tables of chemical potentials of some substances at our disposal.^{2,3,5,7} (See also <http://job-stiftung.de/index.php?id=11,0,0,1,0,0>.)

Is a certain reaction possible, and if so, how much energy is released in a given conversion? Take the case of hydrogen gas and oxygen gas. The reaction that produces water is



Tables of chemical potentials for standard conditions (a temperature of 25°C, a pressure of 1 bar, and a concentration of solutions of 1 M;¹⁴) tell us that the chemical potential of both hydrogen gas (H_2) and oxygen gas (O_2) are zero. The chemical potential of water, on the other hand, is -234 kJ/mol . Now, the overall driving force of a reaction depends on the quantities involved:

$$\begin{aligned} [\Delta\mu]_R &= 1\mu_{\text{H}_2\text{O}} - (1\mu_{\text{H}_2} + 0.5\mu_{\text{O}_2}) \\ &= -273.2 \frac{\text{kJ}}{\text{mole}} - (1 \cdot 0 + 0.5 \cdot 0) \frac{\text{kJ}}{\text{mole}} \end{aligned} \quad (3)$$

If the overall driving force is negative, the reaction occurs spontaneously, and energy is released. Obviously, hydrogen gas and oxygen gas can react spontaneously at 25°C and a pressure of 1 bar, and energy is released. The amount of energy released for 1 mole of H_2 is -273.2 kJ . Here is a second example. What happens to ice at standard conditions? Again, tables of chemical potentials tell us that the potential of ice is higher than that of water (at 25°C). Therefore, ice will spontaneously convert to water.

5 T and P dependence of the chemical potential

The second small example in Section 4 brings up an interesting question. If ice melts at 25°C, what happens at lower temperatures?

Chemical potentials depend on a number of quantities, among them temperature and pressure. In an introductory course, we can treat these dependencies in a simple yet useful manner by using linearizations. We may write

$$\mu(p, T_0) = \mu(p_0, T_0) + \beta(p - p_0) \quad (4)$$

$$\mu(p_0, T) = \mu(p_0, T_0) + \alpha(T - T_0) \quad (5)$$

for the dependence of the potential on pressure (Equation 4) and on temperature (Equation 5). If the pressure and temperature coefficients of the chemical potential (β and α) are known (again for standard conditions), we can perform simple calculations that allow us to understand a range of everyday phenomena.

Take the example of ice and water. At what temperature would ice no longer turn into water? In different words, what is the temperature at which there is an equilibrium of phases? Equilibrium means vanishing chemical driving force, i.e., the difference of the chemical potential is zero:

$$\mu_{\text{water}}(p_0, T) = \mu_{\text{ice}}(p_0, T) \quad (6)$$

Water and ice tell us how to deal with this type of problem:

$$\begin{aligned} \mu_{\text{water}}(p_0, T_0) + \alpha_{\text{water}}(T - T_0) \\ = \mu_{\text{ice}}(p_0, T_0) + \alpha_{\text{ice}}(T - T_0) \end{aligned}$$

Introducing numbers¹⁴ leads to a temperature of 1.5°C for the melting point of ice. For a linear approximation to an otherwise complicated relation, this is not bad.

6 Dilute solutions

The chemical potential obviously depends upon the concentration of a substance in its environment. In the case of solutions, this fact makes the chemical potential of the solvent dependent upon the concentration of the solute. These observations lead to explanations of a host of interesting phenomena.

The dependence upon concentration is most easily considered by noting that the solute in a dilute solution behaves just like an ideal gas (in empty space). For isothermal conditions, the chemical potential of an ideal gas depends upon its pressure as follows:⁹

$$\mu(p, T) = \mu(p_0, T) + RT \ln(p/p_0) \quad (7)$$

Therefore, the chemical potential of a solute must depend upon its concentration as follows:

$$\mu(c, T) = \mu(c_0, T) + RT \ln(c/c_0) \quad (8)$$

Let us now treat a couple of examples to see what can be achieved when we make use of the concept of chemical potential and chemical driving force. First, consider the solution of CO_2 in bottled water. Assume the pressure of the CO_2 in the empty space of a sealed bottle to be 2 bar. How much CO_2 will be dissolved in the water? Again, we can think of this as a case of chemical equilibrium that is established some time after CO_2 has been introduced in the bottle. We have equilibrium when the drive of CO_2 in the water to go into the gaseous phase is equal to the drive of the gas to go into solution. The condition leads to a ratio of $c_{aq}/c_{aq,0} = 0.10$. Therefore, the concentration of CO_2 in water in this bottle is 0.10 mole/L, which corresponds to a little more than 4 g per liter.

Now consider the effect of the solute upon the solvent.⁹ Assume we have a solvent with some solute in an

open container at air pressure. The pressure of the mixture is 1 bar. The solute has a certain pressure which increases with concentration, so the pressure of the solvent decreases. Since the chemical potential of a liquid changes with its pressure, we finally arrive at

$$\mu_1(T, y) = \mu_1(T, 0) - RTy \quad (9)$$

where $y = n_s / (n_l + n_s)$ is the mole fraction of the solute in the solution (s stands for solute, l for solvent or liquid).

This explains some important phenomena such as osmosis or the change of boiling point and melting point of a liquid. Take osmosis as an example. If a red blood cell is placed in fresh water, it absorbs a lot of it. The reason is simply that the pressure of water inside the cell is lower than outside: there are substances dissolved in it.

7 Dynamical models

Transports and chemical reactions are governed by chemical driving forces, i.e., by the difference between chemical potentials in two states. We will show here that transports and reactions can be treated analogously, and that, near equilibrium, transport and reaction equations take the well known forms involving concentrations.

Transports between different environments. If a substance flows in a homogenous environment, the idea of the chemical driving force leads to Fick's law of diffusion. If the environments are different but uniform, we can easily derive the proper constitutive rule for transport between the environments.

Substances flow from one environment into another as long as there is a difference of the chemical potentials of the substance in these environments. If the substance is dissolved, its chemical potential depends logarithmically upon its concentration. Therefore

$$\Delta\mu_{\text{transport}} = \mu_B^{\text{eq}} - \mu_A^{\text{eq}} + RT \ln \left(\frac{c_B}{c_B^{\text{eq}}} \right) - RT \ln \left(\frac{c_A}{c_A^{\text{eq}}} \right) \quad (10)$$

The condition of equilibrium has been chosen as the reference point for calculating the chemical potential. A and B refer to the substance in environments A and B. The difference of chemical potentials in equilibrium must be zero. For small deviations from equilibrium, the expression can be linearized to yield

$$I_n = -Ak(c_A - Kc_B) \quad (11)$$

$$\text{with } c_A^{\text{eq}}/c_B^{\text{eq}} = k \quad (12)$$

where k is an equilibrium constant. Here, A is the surface area through which the substance migrates. Ak may be interpreted as a kind of conductance. The expression in Equation 11 can be generalized to one where the equilibrium relation is not constant, such as for toluene in water and soil. For this example, the term in parentheses in Equation 11 would change to $c_w - kc_s^a$.

Now, we combine this constitutive expression with the law of balance of amount of substance. This yields

$$\frac{dc_A}{dt} = -\frac{1}{V_A} Ak(c_A - Kc_B) \quad (13)$$

where V_A and c_A are the volume of environment A, and the concentration of the substance in that environment, respectively.

A simple reaction. Take the transformation of a substance A into a substance B (or vice-versa). Assuming a reaction rate proportional to the chemical driving force, combining the equation of balance of amount of substance with the constitutive law leads to

$$\frac{dn_A}{dt} = -k'c_A [\Delta\mu]_n \quad (14)$$

Linearization (as in the case of transport treated above) yields the typical kinetic equation

$$\frac{dc_A}{dt} = -k(c_A - Kc_B) \quad (15)$$

Creating a dynamical model. A simple model for the mutarotation of glucose (Figure 3) can be created that can be successfully compared to experimental data.¹⁰ In the case of mutarotation of glucose, it turns out that a relation for the reaction rate that is linear in the chemical driving force yields very good results. Other cases would be different, since chemical reactions show a great variety of behaviors. However, the idea of kinetics dependent upon the chemical driving force remains the simplest starting point for dynamical modeling.

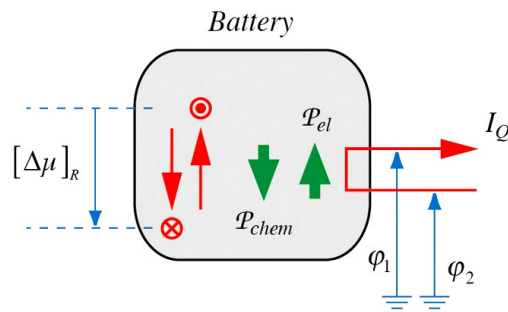


Figure 5. Process diagram of an ideal battery. In the chemical reactions, some substances disappear (down-arrow and symbol of sink) and some are produced (up-arrow and symbol of source). Overall, the reaction runs “downhill” (from higher to lower chemical potentials). As a result, energy is released at a certain rate (vertical fat arrow). The energy release is used (vertical fat arrow pointing up) for driving a flow of electric charge I_Q “uphill” (from lower to higher electric potentials).

8 Conclusions

It has been demonstrated by way of examples that the idea of chemical potentials and the chemical driving force can be introduced early on in a course on chemical dynamics. The results are courses that unify the great variety of chemical processes and deal with chemical phenomena in a much more vivid and intuitive manner than is commonly the case.

The idea of the chemical potential can be introduced in analogy to temperature or electric potential. As in

those cases, a difference of potentials is conceptualized as a driving force for processes (temperature difference for the flow of entropy, voltage for the flow of charge, and chemical potential difference for chemical transports and reactions).

Many concrete examples of chemistry can be treated by employing the assumption that differences of chemical potentials vanish in equilibrium. If we have tables of potentials for substances, and if we know how these potentials depend upon circumstances (temperature, pressure, concentration, environment, etc.), we can perform back-of-the-envelope type of calculations for interesting real-life situations. Finally, applying the idea of the chemical driving force more generally, we can come up with simple dynamical models for transports and reactions (see ref. [9], Chapter 6, 2nd edition).

A type of application not treated here deserves mentioning. We can extend the idea of potentials to combined potentials such as the electro-chemical potential or the gravito-chemical potential and then deal with cases from electrochemistry (including many from biochemistry) or the transport of substances in the gravitational field (including plant physiology and hydrology).

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References

1. Job G., Neudarstellung der Wärmelehre, Die Entropie als Wärme. Akademische Verlagsgesellschaft, Frankfurt (1972).
2. Job G., Das chemische Potential im Physik- und Chemie-Elementarunterricht, Konzepte eines zeitgemäßen Physikunterrichts, Heft 2, Hermann Schroedel Verlag KG, Hannover, p. 67-78 (1978).
3. Job G., Chemische Reaktionen physikalisch beschrieben, Konzepte eines zeitgemäßen Physikunterrichts, Heft 4, Hermann Schroedel Verlag KG, Hannover, p. 14-31 (1981).
4. Job G. and Herrmann F. Chemical potential – a quantity in search of recognition. *Eur. J. Phys.* 27, 353-371 (2006).
5. Rüffler R. and Job G., Chemical Potential From the Beginning. Conference of the International Union of Pure and Applied Chemistry, Torino, Italy. 4-12 August (2007).
6. Job G. and Rueffler R., *Physikalische Chemie*. Teubner Studienbücher Chemie, B. G. Vieweg und Teubner Verlag, Wiesbaden, Germany (2011).
7. Herrmann F., *Der Karlsruher Physik-Kurs*. Sekundarstufe 1 (3 Bände), Sekundarstufe 2 (2 Bände), 2 Lehrerbände. Universität Karlsruhe and Aulis-Verlag, Köln. (1989-1999).
8. Herrmann F. and Wuerfel P., Light with nonzero chemical potential. *Am. J. Phys.* 73, 717-721 (2005).
9. Fuchs H. U., *The Dynamics of Heat*. Springer-Verlag, New York, 2nd Edition (2010).
10. D'Anna M., Fuchs H. U., Lubini P., System dynamics modeling – from mechanics to chemistry. GIREP - MPTL Conference - Nicosia, 18-22 August (2008).
11. Herrmann F., Comencemos con la entropia. *Rev. Cub. Fis.*, to be published in this same number. (2010).
12. Jesse K., Biological Half-Life of Cardiolite. *The Physics Teacher* 46, 522-525 (2008).
13. Fuchs H. U., From Image Schemas to Dynamical Models in Fluids, Electricity, Heat, and Motion. An Essay on Physics Education Research. ZUAS at Winterthur (2007).