

- *Учебни опити и демонстрации* •
- *Teaching Chemical Experiment* •

**THE ECONOMIC DEMONSTRATOR:
PREPARE IT ONCE, USE IT MANY TIMES.
I. CONTINUOUS THERMOCHROMISM
IN THE $\text{NO}_2\text{--N}_2\text{O}_4$ SYSTEM – EQUILIBRIUM
SHIFTS INDUCED BY TEMPERATURE CHANGES**

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Abstract. Chemical equilibrium is characteristic in all cases where the direct and the reverse reaction occur simultaneously. The equilibrium reagent composition can be altered by changing the pressure, the temperature or the concentration of some participants in the reaction. In this paper a lecture demonstration is offered showing the temperature dependent equilibrium between NO_2 and N_2O_4 . It may also serve as an example of continuous thermochromism, owing to the fact that NO_2 is coloured, while N_2O_4 is not. The demonstration is performed in a purpose designed sealed vessel, thus making it both safe and cheap (it may be repeated indefinite number of times with the same equipment). The *RGB* colour arguments of fixed region in a series of photographs were measured as a function of temperature. An absorption function *A*, was introduced on the basis of the colour arguments, its value being proportional to the NO_2 concentration. Finally, a best-fit function was fitted to the pairs of data absorption–temperature using non-linear least squares interpolation.

Keywords: chemical equilibrium, temperature dependence, nitrogen dioxide, dinitrogen tetroxide, lecture demonstration.

Introduction

(1) *The Economic Demonstrator*

Chemical demonstrations might be both time and money consuming. The two mentioned properties are undesirable and are sometimes used as an excuse for not performing chemical demonstrations. In a series of several papers we will introduce a method that is almost ideal for instructors: prepare the equipment for demonstration once, and then use it unlimited number of times. The method is based on sealing the materials in glass tubes or similar vessels. Then changes of the optical properties of the studied materials are induced (typically by heating the vessel) and are discussed in the light of the phenomenon to be presented.

The first phenomenon that we present is devoted to shifts in the equilibrium between nitrogen dioxide (NO_2) and dinitrogen tetraoxide (N_2O_4). The phenomenon is an easy one to follow, owing to the fact that the changes of the equilibrium are followed by continuous colour changes. The phenomenon is in the same time a convincing demonstration of **continuous thermochromism**.

(2) *Thermochromism*

Thermochromism is a phenomenon where certain substances change their colour upon changing the temperature. The colour change has to be **reversible**. There are two types of thermochromism: continuous thermochromism (the colour changes continuously during the temperature change) and discontinuous (the colour changes abruptly at some characteristic temperature). The phenomena of continuous thermochromism are usually related to chemical changes occurring in the system, while those of discontinuous type are either due to phase transition (usually of order-disorder type) or due to isomerisation reaction (like changes in the coordination).

(3) *Chemical Equilibrium*

The phenomenon of chemical equilibrium is well known in literature [1–3] and is taught in many chemistry courses (both undergraduate and graduate). There are a number of experiments [4–6] that have been offered to demonstrate this phenomenon. In this paper a demonstration of the equilibrium phenomenon in a NO_2 – N_2O_4 system is presented emphasizing the temperature influence.

It is known that for some reactions the reactants are not completely exhausted. That is, neither the reactants' concentration drops to zero, nor the products' concentration achieves its maximum possible value [1]. In 1864 Cato Maximilian Guldberg (1836–1902) and Peter Waage (1833–1900) postulated the **law of mass action**, which gives a relationship between the concentrations

of the reactants and products at equilibrium for any reaction [4, 7].

Let us denote a general chemical reaction with the equation



where a , b , c and d are the stoichiometric coefficients, A and B are reactants, C and D are reaction products and the \rightleftharpoons sign represents equilibrium. In such a case, one may introduce a new quantity, K_c , defined as:

$$(2) \quad K_c = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}$$

where the square brackets represent the equilibrium concentrations of the participant in question. K_c is called the **equilibrium constant** (the subscript c indicates that K_c is defined in terms of molar concentrations).

For the purposes of this demonstration, a particular type of chemical reaction (reaction of dimerization) is of particular importance:

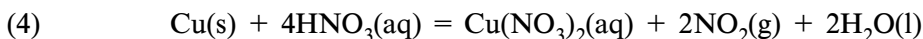


The value of the equilibrium constant at any temperature does not depend on the initial concentrations of reactants and products. It is also irrelevant whether other substances are present, as long as they do not react with either a reactant or a product (the latter substances could be called **spectators**). On the other hand, the value of the equilibrium constant does vary with temperature.

Experimental

(1) Preparation of NO_2

0.5 g of copper grains are put into a side-armed flask connected to a piece of 50 mL pipette. A separation funnel is mounted on the neck of the flask for controlled addition of concentrated nitric acid. Once the acid is added, a vigorous reaction occurs, producing reddish-brown gas (for simplicity we shall call it NO_2). The gas displaces the air from the flask and further fills the pipette. After the pipette is filled with NO_2 it is sealed to form an ampoule. The chemical equation for the gas-generation process is



(2) The Demonstration

The ampoule filled with NO_2 is placed in an appropriate beaker with glycerol and heated until it reaches $128,5^\circ C$. The experimental setup (at room temperature) is given below (cf. Fig. 1).



Figure 1: Shifts in the $\text{NO}_2\text{--N}_2\text{O}_4$ equilibrium — setup for the demonstration.

(3) *Photographs and Colour Analysis*

The photographs were taken on a FUJIFILM *FinePIX4700* digital camera, starting at 128 °C, down to 18 °C with a step of 10 °C (cf. Fig. 2).

In order to gain more quantitative insight into the process, we analyzed the dependence of the colour intensity with temperature in a fixed region of the photographs. The idea for such an approach was introduced elsewhere [8]. This task is really simple when dealing with digital photographs, as the software packages (like Adobe Photoshop [9]) make it possible to read the colour arguments of a single pixel or of a set of pixels (an average value is automatically calculated). For this purpose, the latter approach (i.e. the average *RGB* values) was considered. The argument of any of the colours may vary from 0 (no light) to 255 (maximum light). Thus very intense (dark) colour means that the values of the *RGB* arguments will be relatively low and vice versa.

In order to have physically more acceptable behaviour (i.e. that the higher colour intensity be associated with higher values for the absorption parameters), we first calculated the so-called colour complements, that is $R_c = 255 - R$; $G_c = 255 - G$; $B_c = 255 - B$. Then we calculated the absorption function, A , as the sum of the colour complements ($A = R_c + G_c + B_c$). We actually analyzed the variation of the latter quantity with temperature. The original high-resolution photographs were used for that matter (those given in Fig. 2 are in low resolution, in order to decrease the size of the final document).

The least squares-fit of the intensity—temperature data pairs was performed by WinCurveFit [10].

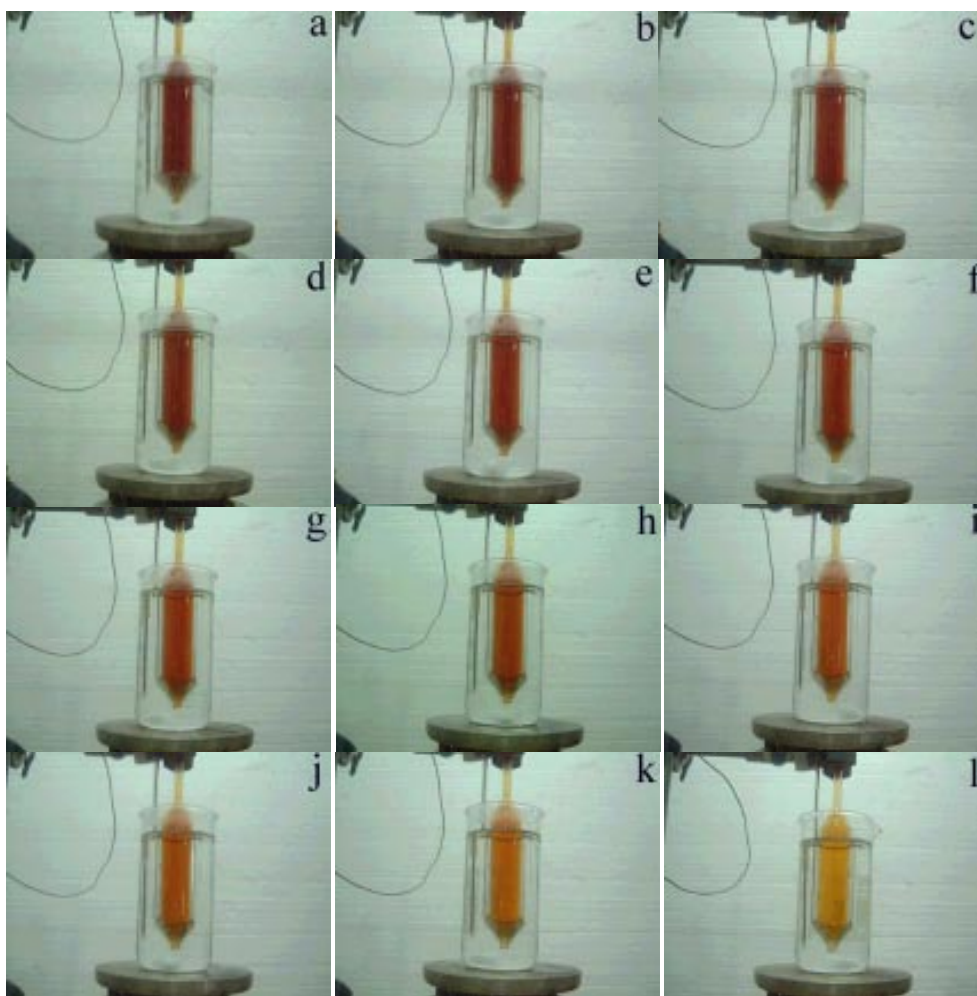


Figure 2. NO_2 concentration decreases, and that of N_2O_4 increases upon cooling:
 a – 128 °C; b – 118 °C; c – 108 °C; d – 98 °C; e – 88 °C; f – 78 °C;
 g – 68 °C; h – 58 °C; i – 48 °C; j – 38 °C; k – 28 °C; l – 18 °C.

(4) *Safety Tips*

The concentration of nitrogen dioxide, as well as the concentrations of other nitrogen oxides in the atmosphere is relatively large due to the combustion of fossil fuels in heating installations and combustion engines. Together with SO_2 and SO_3 they are the major contributor to acid rain. They are also toxic to humans and their inhalation causes breathing difficulties. The most toxic and irritant of all nitrogen oxides is nitrogen dioxide (200 ppm is said to be the lethal air concentration).

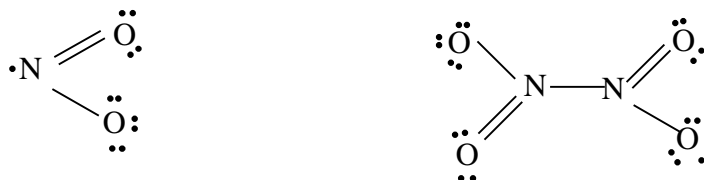
Therefore, the NO_2 generation should always be performed in a hood. The test-tubes/ampoules with NO_2 must be handled with extreme care. Certainly, stirring the liquid in the beaker with vessels filled with NO_2 must be avoided. Tubes with NO_2 should be kept in closed container (styrofoam might be ideal for that matter) in a well ventilated place.

In the case of an accident immediately call for physician. In case of eye contact, flush eyes with water and ask for medical advice.

Discussion

The concept of equilibrium can be best presented in relation to an actual process. The dimerization of NO_2 could be considered as a suitable lecture demonstration because there is an obvious colour change that can easily be followed. Thus the reddish—brown NO_2 transforms into colourless N_2O_4 upon cooling. The opposite process occurs on heating. The colour intensity is thus proportional to the concentration of NO_2 .

The act of dimerization can be defined as bonding together of two identical molecules, the result being a new molecule — a dimer. In the case of NO_2 dimerization, the unpaired electron on each of the NO_2 molecules forms a bond, thereby forming N_2O_4 in which there are no unpaired electrons. For a better notion of the overall process of dimerization, the Lewis' structures of the monomer and the dimer are given below (of course, electron resonance will make the N—O bonds in both compounds equal):



The freshly produced gas in the ampoule mainly consists of NO_2 (and sometimes is simply called nitrogen dioxide, as we did earlier). It is logical that NO_2 is the dominant species, because the reaction between copper and nitric acid is strongly exothermic.

The gas is, actually, a mixture of NO_2 and N_2O_4 at equilibrium. As told earlier, nitrogen dioxide is a dark coloured reddish—brown gas and dinitrogen tetraoxide is a colourless gas. This equilibrium can be represented by the following equation:



According to the literature [5, 6], the reaction enthalpy is $\approx -58 \text{ kJ mol}^{-1}$, meaning it is an exothermic reaction. Therefore, an influx of energy (e.g. via heating) shifts the equilibrium to the left and vice versa. Thus, when an am-

poule containing the equilibrium mixture is put into a hot glycerol, the equilibrium is shifted in the direction of producing more NO_2 and consequently, a gas mixture with more intense colour is obtained. Analogously, upon cooling the amount of nitrogen dioxide decreases, the amount of dinitrogen tetraoxide increases and the colour of the tube fades. One can witness this from the photographs (cf. Fig. 2). This is, by the way, a direct consequence of the **Le Chatelier's principle** which can be formulated as follows: "If any change of conditions is imposed on a system in equilibrium, the system will alter in such a way as to counteract the imposed change [2]".

For a quantitative insight in the equilibrium changes, we further present the variation of the colour arguments with temperature. The input data are given in Table 1, and the results for the non-linear least-squares fit are given in Figure 3.

Table I. Variation of the average values of the *RGB* colour arguments with temperature (note that $A = R_c + G_c + B_c$, i.e. it is calculated from the colour complements)

No.	1	2	3	4	5	6	7	8	9	10	11	12
$t/^\circ\text{C}$	128	118	108	98	88	78	68	58	48	38	28	18
<i>R</i>	83	90	95	96	102	105	115	116	127	133	143	164
<i>G</i>	29	30	31	30	34	32	37	46	51	57	75	111
<i>B</i>	22	21	17	15	22	18	11	8	16	11	13	9
<i>A</i>	631	624	622	624	607	610	602	595	571	564	524	481

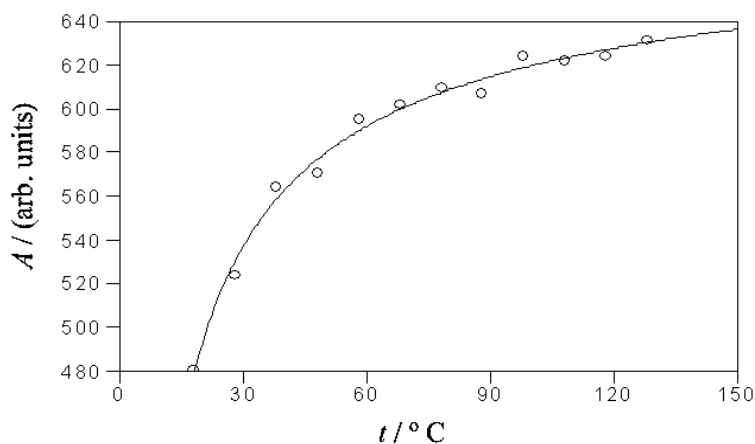
One should always keep in mind that the higher the *A* values, the more NO_2 is present in the equilibrium mixture.

The pairs of *A*, *t* values were plotted and the non-linear least-squares fit was performed with a hyperbolic-like type function of the form (cf. Fig. 3):

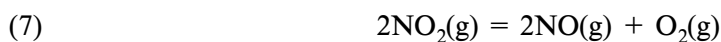
$$(6) \quad A = a - \frac{b}{(t/^\circ\text{C})^c}$$

where $a = 694.7 \pm 23.0$; $b = 1283 \pm 321$ and $c = 0.617 \pm 0.118$ are the least squares best-fit parameters. The regression coefficient ($R^2 = 0.990$) is more than satisfactory.

The behaviour of the function is obviously feasible: *A* (and hence, the NO_2 concentration) increases with temperature. This function, one has to say, is just a numerical interpolation function. It has no real physical significance. For ex-



ample, the function predicts that A exhibits asymptotical behaviour at high temperatures. In reality, for temperatures above 200 °C [11], another chemical reaction occurs:



that will make the concentration of NO_2 decrease. Surely, the measurements ended well below this temperature, so the computer program ‘has no idea’ about the behaviour of the system.

The experiment is known in several (simpler) versions [12–14]. All of these versions are more or less qualitative, allowing the observer to witness that the NO_2 concentration increases or decreases upon temperature/pressure changes. In the present experiment, we offered one more (quantitative) point, taking advantage of the opportunities enabled by computers and digital cameras.

Conclusion

This demonstration illustrates shifts in equilibrium in the $\text{NO}_2\text{—N}_2\text{O}_4$ system. It could be used as a lecture demonstration, but one must keep in mind that it is a bit lengthy so some modifications might be important (e.g. once the maximum temperature is attained, the ampoule may be removed from the hot bath, thus allowing much faster cooling). The *RGB* colour arguments were analyzed as a function of temperature and feasible results were obtained for the variation of the NO_2 concentration with temperature.

References and notes

1. www.iupac.org/didac (accessed March 15th 2006).
2. Glinka, N. L. *General Chemistry*, Vol. 1, Mir Publishers (English translation), Moscow, 1986, pp. 196–200.
3. Brady, J. E. *General Chemistry: Principles and Structure*, John Wiley & Sons, New York, 1990, pp. 496–500.

4. <http://cwx.prenhall.com/bookbind/pubbooks/blb/chapter15/medialib/blb1502.html> (accessed March 15th 2006).
5. <http://www.pc.chemie.uni-siegen.de/pci/versuche/english/v62-1.html> (accessed March 15th 2006).
6. http://www.chem.umn.edu/services/lecturedemo/info/NO2_Equilibrium.html (accessed March 15th 2006).
7. Brady, J. E. *General Chemistry: Principles and Structure*, John Wiley & Sons, New York, 1990, pp. 485–486.
8. M. Najdoski, Lj. Pejov, M. Monković, V. M. Petruševski, to be published.
9. Adobe Photoshop version 7.0, © 1990–2002, Adobe Systems Incorporated, 2002.
10. WinCurveFit version 1.1.8, ©1991–2002, Kevin Raner Software, June 2002.
11. E. Wiberg, *Lehrbuch der anorganischen chemie*, Školska knjiga, Zagreb, 1967, pp. 268–269 (translation from German into Croatian).
12. V. N. Verhovskii, *Techniques and Methods of Performing Chemistry Experiments in a College*, Volume 2, Zavod za izdavanje udžbenika SR Srbije, Beograd, 1965, pp. 144–145 (translation from Russian into Serbian).
13. Z. Yang, *J. Chem. Educ.* **70**, 94–95 (1993).
14. B. Z. Shakhshiri, *Chemical Demonstrations: A Handbook of Teachers of Chemistry*, The Wisconsin University Press, Madison, WI, 1985, Vol. 2, pp. 180–183.

ХИМИЧНИ ДЕМОСТРАЦИИ: ТЕРМОХРОМИЗЪМ В РЕАКЦИЯТА $\text{NO}_2/\text{N}_2\text{O}_4$ – ИЗМЕСТВАНЕ НА РАВНОВЕСИЕТО С ПРОМЯНА НА ТЕМПЕРАТУРАТА

Резюме. Равновесният реакционен състав се променя при промени в налягането, температурата и концентрацията на някои от реагентите в химическата система. В тази статия се предлагат опити с реакцията между NO_2 и N_2O_4 , където въпросните промени предизвикват явлението термохромизъм. Всъщност тази реакция и досега е често използвана за демонстрационни цели. Тук обаче се предлагат някои технически и методични подобрения, които разкриват нови възможности на учебния химичен експеримент.

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