

EQUILIBRIA OF THE REACTIONS BETWEEN NITROGEN OXIDES AND THE SODIUM CARBONATE

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A general analysis of chemical equilibria in a system consisting of the gaseous nitrogen monoxide, nitrogen dioxide, carbon dioxide, oxygen and of the solid sodium carbonate is carried out with respect to the equilibrium partial pressures of nitrogen oxides. The pertaining equations are derived for three regions of existence of the above system. The results are represented graphically and discussed from the point of view of removing the nitrogen oxides from the waste gases.

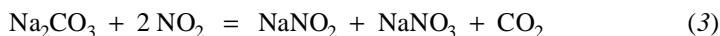
The contemporary human activities are accompanied by a production of huge amounts of waste gases containing undesirable components, from which the oxides of sulfur and nitrogen are to be named in the first place. One of the ways how to render them harmless, is to neutralize these acid compounds by means of basic solid such as reactive oxides or carbonates of metals. To evaluate the feasibility of such methods, it is desirable to carry out a thermodynamic analysis of pertinent reactions, which yields the equilibrium conditions limiting the process. A general analysis of systems containing the sulfur dioxide has been carried out long ago¹, and in this paper we are dealing with the equilibria of reactions between nitrogen oxides and sodium carbonate in the presence of carbon dioxide and oxygen, which form usual constituents of the waste gases.

GENERAL PART

From all the nitrogen oxides, we will take into consideration only monoxide NO and the dioxide NO₂, since the above oxides represent usually the majority components of gases².

In a system consisting of nitrogen oxides and the sodium carbonate, the following reactions may take place in the presence of oxygen.





It can be found, however, that only three from the above five equations are independent, and the remaining two equations can be expressed in terms of the first named ones. From the point of view of equilibrium, of course, it is irrelevant which equations are selected as independent and which are dependent ones. Thus, from the above five equations, it is possible to form nine sets of three independent equations as follows.

<i>(1)</i>	<i>(2)</i>	<i>(3)</i>	<i>(1)</i>	<i>(3)</i>	<i>(5)</i>	<i>(2)</i>	<i>(3)</i>	<i>(5)</i>
<i>(1)</i>	<i>(2)</i>	<i>(5)</i>	<i>(2)</i>	<i>(4)</i>	<i>(5)</i>	<i>(2)</i>	<i>(4)</i>	<i>(5)</i>
<i>(1)</i>	<i>(3)</i>	<i>(4)</i>	<i>(2)</i>	<i>(3)</i>	<i>(4)</i>	<i>(3)</i>	<i>(4)</i>	<i>(5)</i>

Here it is to be noted, that the number of combinations of three equations from the total number of five is equal to $\binom{5}{3} = 10$, i.e. that there should exist ten combinations and not nine as above. In the given case, however, there exist really only nine, since the combination *(1) (2) (4)* does not contain one of the compounds, i.e. the sodium nitrate, so that it is not possible by means of this combination to express other combinations containing the nitrate. Further on, it can be remarked, that the system of basic equations is not limited to five, as given above, i.e. that the basic set may be extended by means of additional equations and this extending is accompanied by increasing the number of triad combinations. For example by adding one equation, the theoretical number of triads increases from ten to twenty. Finally, it may be added, that the selection of the set of three independent equations is a matter of convenience.

In the following, we will start with the system of first three equations, i.e. with the Eqs *(1)*, *(2)*, and *(3)*. If we are studying such a system from the point of view of equilibrium partial pressures of nitrogen oxides, and if the solid phases are present in the pure state, we can distinguish in this system three regions of existence, which will be denoted as *A*, *B*, and *C*.

A. In the first of them, the partial pressures of all the gaseous components assume their equilibrium values. From the equilibrium conditions of Eqs *(2)* and *(3)*, we obtain

expressions for the partial pressures of nitrogen monoxide P_{NO} and of nitrogen dioxide P_{NO_2} in the forms

$$P_{\text{NO}} = (P_{\text{CO}_2})^{1/2} K_3^{1/2} / K_2 \quad (6A)$$

and

$$P_{\text{NO}_2} = (P_{\text{CO}_2})^{1/2} K_3^{1/2}, \quad (7A)$$

where K_2 and K_3 are equilibrium constants of Eqs (2) and (3), and P_{CO_2} is the partial pressure of carbon dioxide. Therefrom, a relation for the partial pressure of nitrogen oxides P_{NO_x} follows in the form

$$P_{\text{NO}_x} = 1/K_3^{1/2} [K_3/K_2 + 1] (P_{\text{CO}_2})^{1/2}, \quad (8A)$$

where $P_{\text{NO}_x} = P_{\text{NO}} + P_{\text{NO}_2}$ in accord with what has been said above. Additionally, the fraction of nitrogen monoxide from both nitrogen oxides can be expressed from the Eqs (6A) and (8A) as

$$P_{\text{NO}}/P_{\text{NO}_x} = K_3/(K_2 + K_3). \quad (9A)$$

At first sight, the results given above contain somewhat astonishing feature. Namely, the relations (6A), (7A), and (8A) do not include the partial pressure of oxygen, although the oxygen represents one of the reactants in the Eq. (1). According to the phase law the region A is divariant, so that we may choose here only two variables as independent, for example temperature and partial pressure of carbon dioxide, in agreement with the Eqs (6A), (7A), and (8A). Here the presence of partial pressure of oxygen would represent the third independent variable, and this is inadmissible from the point of view of the phase law. This formal explanation is certainly correct, but a better physical insight into this situation is probably desirable. This is offered by the equilibrium in Eq. (5), from which a relation follows

$$(P_{\text{O}_2})^{1/2} = 1/K_5. \quad (10A)$$

Here K_5 denotes the equilibrium constant of Eq. (5) and is a function of temperature only. Accordingly, the equilibrium partial pressure of oxygen is a function of tempera-

ture only, and does not represent any third independent variable. The reader, however, could object to this, that the Eq. (1) has not been used at all in deriving the Eqs (6A), (7A), and (8A). This is certainly true, but from the equilibrium condition of reaction (1) we obtain a relation

$$P_{\text{NO}} = [1/K_1^{1/2}] (P_{\text{CO}_2})^{1/2} / (P_{\text{O}_2})^{1/4} \quad (11A)$$

any by combining with the Eq. (10A) we have

$$P_{\text{NO}} = (K_5/K_1)^{1/2} (P_{\text{CO}_2})^{1/2}. \quad (12A)$$

It is easy to show, that the Eq. (5) can be expressed in terms of the Eqs (1), (2), and (3), namely as

$$(5) = (1) + (3) - 2(2), \quad (13A)$$

or in terms of equilibrium constants as

$$K_5 = K_1 K_3 / K_2^2. \quad (14A)$$

By substituting the expression (14A) into (12A) we arrive at a relation

$$P_{\text{NO}} = K_3^{1/2} (P_{\text{CO}_2})^{1/2} / K_2, \quad (15A)$$

which is identical with the Eq. (6A). Thereby it is shown, that we need not start with the Eq. (2), but we can start with the Eq. (1), and arrive by alternative procedure at the same result.

It can be concluded, that in the region A the equilibrium partial pressure of nitrogen oxides are dependent on two independent variables, e.g. on temperature and partial pressure of carbon dioxide.

B. In the second region the partial pressure of oxygen is lower than the equilibrium one, so that the reaction (5) is quantitatively shifted to the left side, and therefore the nitrate cannot exist in the system. From the equilibrium conditions of Eqs (1) and (2),

we obtain the following relations for the partial pressures of nitrogen oxides in the forms

$$P_{\text{NO}} = [1/K_1^{1/2}] (P_{\text{CO}_2})^{1/2} / (P_{\text{O}_2})^{1/4} \quad (6B)$$

$$P_{\text{NO}_2} = [K_1^{1/2}/K_2] (P_{\text{O}_2})^{1/4} (P_{\text{CO}_2})^{1/2} \quad (7B)$$

and

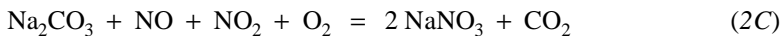
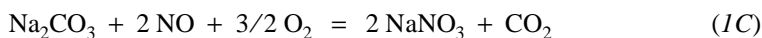
$$P_{\text{NO}_x} = [1/K_1^{1/2}] [1 + (P_{\text{O}_2})^{1/2} K_1/K_2] (P_{\text{CO}_2})^{1/2} / (P_{\text{O}_2})^{1/4} . \quad (8B)$$

It is seen from these expressions, that the partial pressures of nitrogen oxides are dependent on three independent variables, namely on temperature, partial pressure of carbon dioxide, and on partial pressure of oxygen. This conclusion is in agreement with the phase law, according to which the system is trivariant, since in the region *B* the nitrate is absent. In this case the fraction of nitrogen monoxide from both nitrogen oxides assumes the following form

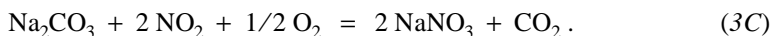
$$P_{\text{NO}}/P_{\text{NO}_x} = K_2/[K_2 + K_1 (P_{\text{O}_2})^{1/2}] . \quad (9B)$$

Similarly as previously, it is possible to arrive at the same result from other starting equations with respecting the condition that the partial pressure of oxygen is lower than the equilibrium one.

C. In the third region the partial pressure of oxygen is higher than the equilibrium one, so that the reaction (5) is quantitatively shifted to the right side, and therefore the nitrite cannot exist in the system. By using this condition, we can transform the Eqs (1), (2), and (3) into



and



These three equations are not independent, and a relation is valid among them

$$(1C) + (3C) = 2(2C), \quad (4C)$$

so that it is sufficient to select two of them to describe the system. Thus, from the equilibrium conditions of Eqs (1C) and (3C), we obtain the following simple expressions for the partial pressures of nitrogen oxides in the forms

$$P_{\text{NO}} = [1/K_{1C}^{1/2}] (P_{\text{CO}_2})^{1/2} / (P_{\text{O}_2})^{3/4} \quad (5C)$$

$$P_{\text{NO}_2} = [1/K_{3C}^{1/2}] (P_{\text{CO}_2})^{1/2} / (P_{\text{O}_2})^{1/4} \quad (6C)$$

and

$$P_{\text{NO}_x} = [1/K_{3C}^{1/2}] [(K_{3C}/K_{1C})^{1/2} 1/(P_{\text{O}_2})^{1/2} + 1] (P_{\text{CO}_2})^{1/2} / (P_{\text{O}_2})^{1/4}, \quad (7C)$$

where K_{1C} and K_{3C} are equilibrium constants of the reactions (1C) and (3C). As it is seen, the partial pressures of nitrogen oxides depend on three independent variables, similarly as in the region *B*, since according to the phase law the system is again trivariant (owing to the absence of the nitrite). In this case, the fraction of nitrogen monoxide from both nitrogen oxides assumes the following form

$$P_{\text{NO}}/P_{\text{NO}_x} = K_{3C}^{1/2} / [K_{3C}^{1/2} + K_{1C}^{1/2} (P_{\text{O}_2})^{1/2}]. \quad (8C)$$

It is of course possible to express the Eqs (5C), (6C), and (7C) in terms of original equilibrium constants by using the following relations

$$K_{1C} = K_1^3 K_3^2 / K_2^4 \quad (9C)$$

and

$$K_{3C} = K_1 K_3^2 / K_2^2, \quad (10C)$$

but the resulting relations have somewhat more complicated forms.

From the analysis given above, the following general conclusions may be drawn about the effect of carbon dioxide and of oxygen on the equilibrium partial pressure of nitrogen oxides above the sodium carbonate.

The carbon dioxide enhances the fugacity of nitrogen oxides in general. This quantity increases proportionally with the square root of the partial pressure of carbon dioxide, and this effect is the same on both nitrogen oxides and in all three regions of existence. There is no influence of carbon dioxide on the relative amount of nitrogen monoxide, since the effects on both nitrogen oxides cancel out one another. Owing to the square root, the effect of carbon dioxide on nitrogen oxides is smaller than an analogous effect on the sulfur dioxide studied previously¹, where the first power appeared.

The effect of oxygen is more complicated, and it depends both on the kind of nitrogen oxide and on the region of existence. In the region *A*, where the partial pressure of oxygen depends on temperature only, no explicit influence of oxygen on the nitrogen oxides is found. In the region *B*, where the partial pressure of oxygen is lower than its equilibrium value, the effect of oxygen on both nitrogen oxides is different: the fugacity of the nitrogen monoxide decreases with the fourth root of the partial pressure of oxygen, in contrast with the fugacity of the nitrogen dioxide which is increasing with the same rate. In the region *C*, where the partial pressure of oxygen exceeds that of equilibrium, the effect of oxygen on both nitrogen oxides is qualitatively the same, i.e. the fugacities of the nitrogen monoxide and of the nitrogen dioxide are decreasing, and the exponent is equal to three quarters in former case, and to one quarter in the latter case. The effect of oxygen on the partial pressure of nitrogen oxides, P_{NO_x} , is a combination of the partial effects mentioned above, in both the *B* and the *C* regions. The relative amount of the nitrogen monoxide decreases with the square root of the partial pressure of oxygen. Generally speaking, the effect of oxygen is smaller than that of the carbon dioxide.

SPECIAL PART

We have calculated the equilibrium constants K_i of reactions (1), (2), (3), (4), (5), (1C) and (3C) from a simplified equation

$$\ln K_i = -\Delta H_i^0/RT + \Delta S_i^0/R. \quad (6)$$

Here ΔH_i^0 and ΔS_i^0 are the standard changes of enthalpy and entropy of the *i*-th reaction at 25 °C. In this equation, the higher members containing the change of heat capacities were neglected, since it has been found, that the deviation in K_i caused by the error in ΔH_i^0 exceed many times the deviation caused by neglecting the higher members, in a

similar way as previously³. To calculate the values of ΔH_i^0 and ΔS_i^0 , the thermodynamic quantities were taken from the source⁴, and to estimate the missing value of heat capacity of the sodium nitrite, we have extended the method proposed previously³. The values of ΔH_i^0 and ΔS_i^0 are given in Table I and the calculated dependences of equilibrium constants are represented in Fig. 1, where the coordinates were selected so that the resulting dependences are linear. At temperatures above three hundred degrees centigrade, the values of K_i are somewhat uncertain, since in this temperature range the sodium nitrite and nitrate are melting. For the sake of illustration, the equilibrium partial pressure of nitrogen oxides P_{NO_x} in all three regions of existence were calculated from Eqs (8A), (8B), and (7C), and typical results are graphically represented in Figs from 2 to 5. In these figures, the area between the dotted straight lines *a* and *d* represents the range of possible practical applications i.e. the range between 10^{-1} and 10^{-4} volume percents of nitrogen oxides in the gas.

DISCUSSION

The situation in region A, where the partial pressure of oxygen assumes the equilibrium value, is shown in Fig. 2. It is evident that on increasing the content of carbon dioxide

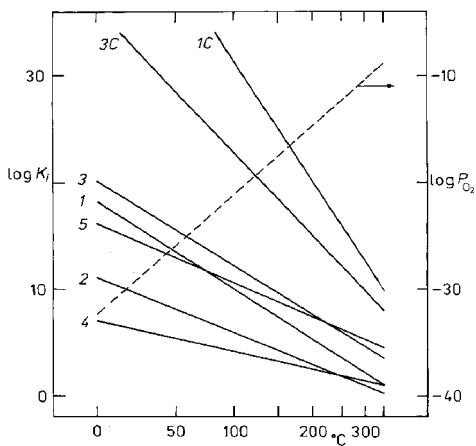


FIG. 1

The temperature dependence of equilibrium constants K_i and of the equilibrium partial pressure of oxygen P_{O_2} in the region A. 1 K_1 , 2 K_2 , 3 K_3 , 4 K_4 , 5 K_5 , (1C) K_{1C} , (3C) K_{3C} . The dotted line represents the P_{O_2} with scale on the right hand side

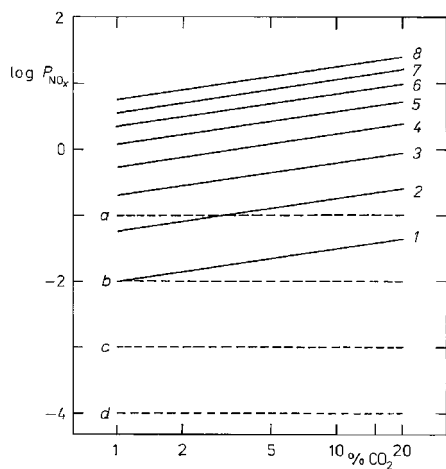


FIG. 2

The effect of carbon dioxide and temperature on the equilibrium partial pressure of nitrogen oxides P_{NO_x} in the region A. % CO_2 : volume percents of carbon dioxide in the gas. Temperature (in $^{\circ}\text{C}$): 1 0, 2 50, 3 100, 4 150, 5 200, 6 250, 7 300, 8 350. The dotted lines represent the volume percents of nitrogen oxides: *a* 10^{-1} , *b* 10^{-2} , *c* 10^{-3} , *d* 10^{-4}

TABLE I
Values of the thermodynamic quantities ΔH_i^0 and ΔS_i^0 in Eq. (6)

Reaction	$-\Delta H_i^0/R$ grad	$\Delta S_i^0/R$
(1)	19 282	-28.706
(2)	12 425	-19.897
(3)	18 692	-21.884
(4)	6 864	-8.810
(5)	13 134	-10.804
(1C)	45 554	-50.309
(3C)	31 826	-32.685

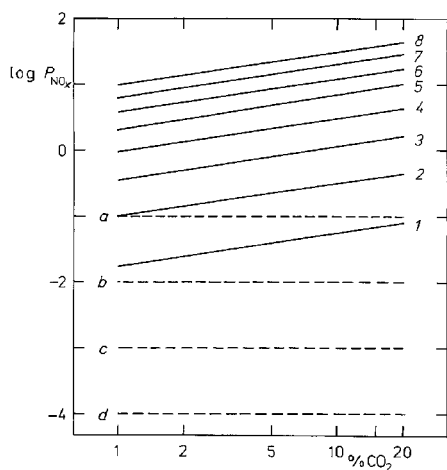


FIG. 3

The effect carbon dioxide and temperature on the equilibrium partial pressure of nitrogen oxides P_{NO_x} in the region B at the partial pressure of oxygen $P_{O_2} = (P_{O_2})_e/10$. % CO_2 : volume percents of carbon dioxide in the gas. Temperature (in $^{\circ}C$): 1 0, 2 50, 3 100, 4 150, 5 200, 6 250, 7 300, 8 350. The dotted lines represent the volume percents of nitrogen oxides: a 10^{-1} , b 10^{-2} , c 10^{-3} , d 10^{-4}

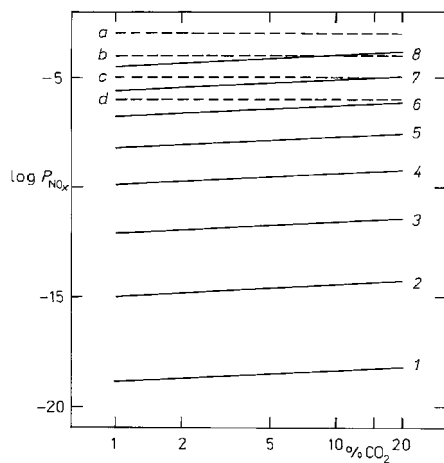


FIG. 4

The effect of carbon dioxide and temperature on the equilibrium partial pressure of nitrogen oxides P_{NO_x} in the region C at the partial pressure of oxygen $P_{O_2} = 0.05$. % CO_2 : volume percents of carbon dioxide in the gas. Temperature (in $^{\circ}C$): 1 0, 2 50, 3 100, 4 150, 5 200, 6 250, 7 300, 8 350. The dotted lines represent the volume percents of nitrogen oxides: a 10^{-1} , b 10^{-2} , c 10^{-3} , d 10^{-4}

from one to twenty percents, i.e. twenty times, the partial pressure of nitrogen oxides increases only about four times, and this increase is the same at all temperatures. The most important result, following from this figure, however, consists in the fact, that the equilibrium partial pressures of nitrogen oxides exceed considerably the range between the dotted lines from *a* to *d*, so that the practical application cannot be taken into consideration in this case.

In the region *B*, the main features of the dependence on carbon dioxide are almost the same as in the region *A*. This is apparent from Fig. 3, from which it is evident that the partial pressures of nitrogen oxides are even somewhat higher, so that the situation is more unfavourable from the view of practical utilization. Here, the partial pressure of oxygen equals to one tenth of the equilibrium value. The dependence of the equilibrium partial pressure of oxygen on temperature is represented in the Fig. 1 by a dotted line with the scale on the right hand side, from which it is seen that the equilibrium values of oxygen partial pressure are ranging from 10^{-30} to 10^{-10} . These values correspond to concentrations of oxygen lower than one part per billion, so that we can summarize the situation in the following way. Practical use of the sodium carbonate for removing the nitrogen oxides from gases is feasible neither in the region *A* nor in the region *B*, not only because of too high partial pressures of nitrogen oxides, but also owing to the extremely low oxygen concentrations in both these regions.

In the region *C*, the situation is illustrated by means of two figures. In Fig. 4, the dependence of partial pressures of nitrogen oxides on the carbon dioxide concentration and on the temperature is represented at a constant partial pressure of oxygen equal to 0.05. The course of both dependences is similar to those in Fig. 2 and Fig. 3 with one important exception, namely, that here the values of partial pressures of nitrogen oxides

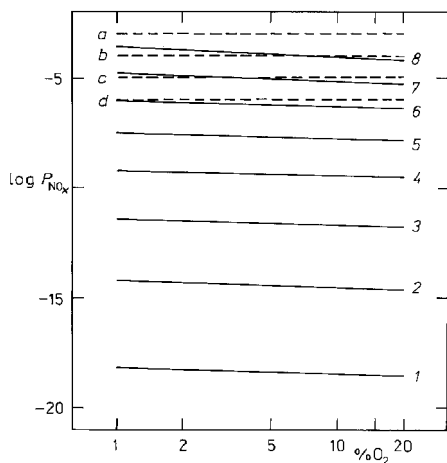


FIG. 5

The effect of oxygen and temperature on the equilibrium partial pressure of nitrogen oxides P_{NO_x} in the region *C* at the partial pressure of carbon dioxide $P_{\text{CO}_2} = 0.10$. % O_2 : volume percents of oxygen in the gas. Temperature (in $^{\circ}\text{C}$): 1 0, 2 50, 3 100, 4 150, 5 200, 6 250, 7 300, 8 350. The dotted lines represent the volume percents of nitrogen oxides: *a* 10^{-1} , *b* 10^{-2} , *c* 10^{-3} , *d* 10^{-4}

are substantially lower, so that appear bellow the range from a to d . In Fig. 5 an analogous dependence on the oxygen concentration is shown at a constant partial pressure of carbon dioxide equal to 0.10. The partial pressure of nitrogen oxides decreases with increasing the oxygen concentration, but this decrease is weaker than the analogous increase with the carbon dioxide concentration in Fig. 4 (approximately one half). It is seen from both these figures, that in the region C the partial pressure of nitrogen oxides is very low particularly in the range from 1 to 20% of carbon dioxide or oxygen. Fortunately, this range represents typical conditions prevailing in the waste gases, so that we may conclude that the use of sodium carbonate for removing nitrogen oxides from gases appears as promising from the thermodynamic point of view. For illustration, at temperatures up to 250 °C, the theoretical degree of nitrogen oxides removal exceeds ninety nine percents.

REFERENCES

1. Erdos E.: Collect. Czech. Chem. Commun. 27, 2152 (1962).
2. Hjalmarsson A. K.: *NO_x Control Technologies for Coal Combustion*, p. 17. I.E.A. Coal Research 24, London 1990.
3. Erdos E.: Collect. Czech. Chem. Commun. 27, 2273 (1962).
4. R. C. West (Ed.): *CRC Handbook of Chemistry and Physics*. CRC Press, Boca Raton 1987.

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