EQUILIBRIA OF REACTIONS BETWEEN NITROGEN OXIDES AND CALCIUM HYDROXIDE

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A general analysis of chemical equilibria in a system consisting of the gaseous nitrogen monoxide, nitrogen dioxide, water vapor, carbon dioxide, oxygen, and the solid calcium hydroxide is carried out with respect to the equilibrium partial pressures of nitrogen oxides. The conditions are defined, under which the calcium hydroxide is transformed to the calcium carbonate. The corresponding equilibrium equations are derived for all nine regions of existence of described system. The results are illustrated graphically and discussed from the point of removing the nitrogen oxides from waste gases.

As a continuation of the previous work[1], the equilibria of reactions between nitrogen oxides and calcium hydroxide in the presence of water vapor, oxygen, and carbon dioxide are studied.

GENERAL PART

In a system consisting of nitrogen oxides[1] and of the calcium hydroxide, the following reactions can take place in the presence of oxygen and carbon dioxide.

$$Ca(OH)_2 + 2\ NO + 1/2\ O_2 = Ca(NO_2)_2 + H_2O \qquad (A)$$

$$Ca(OH)_2 + NO + NO_2 = Ca(NO_2)_2 + H_2O \qquad (B)$$

$$Ca(OH)_2 + 2\ NO_2 = 1/2\ Ca(NO_2)_2 + 1/2\ Ca(NO_3)_2 + H_2O \qquad (C)$$

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O \qquad (D)$$

$$CaCO_3 + 2\ NO + 1/2\ O_2 = Ca(NO_2)_2 + CO_2 \tag{E}$$

$$CaCO_3 + NO + NO_2 = Ca(NO_2)_2 + CO_2 \tag{F}$$

$$CaCO_3 + 2\ NO_2 = 1/2\ Ca(NO_2)_2 + 1/2\ Ca(NO_3)_2 + CO_2 \tag{G}$$

$$1/2\ Ca(NO_2)_2 + 1/2\ O_2 = 1/2\ Ca(NO_3)_2 \tag{H}$$

Only four from the above eight equations are independent. The remaining equations can be expressed in terms of the first ones.

$$(E) = (A) - (D) \tag{1}$$

$$(F) = (B) - (D) \tag{2}$$

$$(G) = (C) - (D) \tag{3}$$

$$(H) = (A) + (C) - 2\ (B) \tag{4}$$

In the whole set of reactions from (*A*) to (*H*), the reaction (*D*) assumes an exceptional position. If the ratio of partial pressures of water vapor and of carbon dioxide P_{H_2O}/P_{CO_2} in the gas phase is higher than the equilibrium constant K_D, the reaction (*D*) is shifted to the left side, so that the calcium carbonate does not exist in the system and the process can be described by the reactions (*A*), (*B*), (*C*) and (*H*), respectively. In the opposite case, when the ratio is lower than K_D, the reaction (*D*) is shifted to the right side, so that the calcium hydroxide does not exist in the system and the process can be described by the reactions (*E*), (*F*), (*G*) and (*H*), respectively. There is still the third case, where the ratio is equal to K_D, so that both the hydroxide and the carbonate coexist in the system. We will treat all those three cases separately and denote them as 1, 2, and 3.

1. *The Calcium Carbonate is Absent*

We may distinguish among three regions according to the partial pressure of oxygen P_{O_2} with regard to the reaction (*H*). We will denote these regions as 11, 12, and 13.

Region 11. The partial pressure of oxygen corresponds to the equilibrium value in the reaction (*H*). From the equilibrium conditions of reactions (*B*) and (*C*), we obtain the expressions for the partial pressure of nitrogen monoxide P_{NO} as

$$P_{NO} = (K_C^{1/2}/K_B)\, P_{H_2O}^{1/2} \;, \tag{5}$$

for the partial pressure of nitrogen dioxide P_{NO_2}

$$P_{NO_2} = K_C^{-1/2}\, P_{H_2O}^{1/2} \;, \tag{6}$$

for the partial pressure of nitrogen oxides P_{NO_x}

$$P_{NO_x} = K_C^{-1/2}\, [(K_C/K_B) + 1]\, P_{H_2O}^{1/2} \;, \tag{7}$$

and for the fraction of nitrogen monoxide from both nitrogen oxides

$$P_{NO}/P_{NO_x} = K_C/(K_B + K_C) \;. \tag{8}$$

Here, the K_B and K_C are equilibrium constants of reactions (*B*) and (*C*), and P_{H_2O} is the partial pressure of water vapor.

The system is divariant and the equilibrium partial pressure of nitrogen oxides is dependent on two independent variables, e.g. on temperature and partial pressure of water vapor. For a more detailed discussion of the situation see ref.[1].

Region 12. The partial pressure of oxygen is lower than at the equilibrium, hence the reaction (*H*) is quantitatively shifted to the left side, and the nitrate cannot exist in the system. Starting from the reactions (*A*) and (*B*), we obtain the corresponding relations in the form

$$P_{NO} = K_A^{-1/2}\, P_{H_2O}^{1/2}/P_{O_2}^{1/4} \;, \tag{9}$$

$$P_{NO_2} = (K_A^{1/2}/K_B)\, P_{H_2O}^{1/2}\, P_{O_2}^{1/4} \;, \tag{10}$$

$$P_{NO_x} = K_A^{-1/2}\,[1 + (K_A/K_B)\,P_{O_2}^{1/2}]\,P_{H_2O}^{1/2}/P_{O_2}^{1/4}\ , \tag{11}$$

and

$$P_{NO}/P_{NO_x} = K_B/(K_B + K_A P_{O_2}^{1/2})\ . \tag{12}$$

The system is trivariant and we can select e.g. the temperature, the partial pressure of water vapor and partial pressure of oxygen as independent variables.

Region 13. The partial pressure of oxygen is higher than at the equilibrium hence the reaction (*H*) is quantitatively shifted to the right side, and the nitrite cannot exist in the system. By using this condition, the equations (*A*) and (*C*) can be transformed into

$$Ca(OH)_2 + 2\ NO + 3/2\ O_2 = Ca(NO_3)_2 + H_2O \tag{K}$$

$$Ca(OH)_2 + 2\ NO_2 + 1/2\ O_2 = Ca(NO_3)_2 + H_2O\ , \tag{L}$$

where the following relations are valid

$$(K) = 3\ (A) + 2\ (C) - 4\ (B) \tag{13}$$

$$(L) = (A) + 2\ (C) - 2\ (B)\ . \tag{14}$$

From the equations (*K*) and (*L*), we obtain the expressions

$$P_{NO} = K_K^{-1/2}\,P_{H_2O}^{1/2}/P_{O_2}^{3/4} \tag{15}$$

$$P_{NO_2} = K_L^{-1/2}\,P_{H_2O}^{1/2}/P_{O_2}^{1/4} \tag{16}$$

$$P_{NO_x} = K_L^{-1/2}\,[(K_L/K_K)^{1/2}\,P_{O_2}^{-1/2} + 1]\,P_{H_2O}^{1/2}/P_{O_2}^{1/4} \tag{17}$$

$$P_{\mathrm{NO}}/P_{\mathrm{NO}_x} = K_L^{1/2}/(K_L^{1/2} + K_K^{1/2}\,P_{\mathrm{O}_2}^{1/2})\ . \tag{18}$$

The system is trivariant again.

2. *The Calcium Hydroxide is not Present*

We can distinguish again three regions of existence of the system, according to the partial pressure of oxygen with regard to the reaction (*H*). We will denote these regions as 21, 22, and 23, and equilibrium oxygen pressure of the reaction (*H*) as $(P_{\mathrm{O}_2})_{\mathrm{e}}$. By a procedure analogous to that given above, we arrive at the following relations.

Region 21. It is characterized by the condition $P_{\mathrm{O}_2} = (P_{\mathrm{O}_2})_{\mathrm{e}}$ and following set of equations can be derived

$$P_{\mathrm{NO}} = (K_G^{1/2}/K_F)\,P_{\mathrm{CO}_2}^{1/2} \tag{19}$$

$$P_{\mathrm{NO}_2} = K_G^{-1/2}\,P_{\mathrm{CO}_2}^{1/2} \tag{20}$$

$$P_{\mathrm{NO}_x} = K_G^{-1/2}\,[(K_G/K_F) + 1]\,P_{\mathrm{CO}_2}^{1/2} \tag{21}$$

$$P_{\mathrm{NO}}/P_{\mathrm{NO}_x} = K_G/(K_F + K_G)\ . \tag{22}$$

Region 22. Here the condition $P_{\mathrm{O}_2} < (P_{\mathrm{O}_2})_{\mathrm{e}}$ gives rise to the equations

$$P_{\mathrm{NO}} = K_E^{-1/2}\,P_{\mathrm{CO}_2}^{1/2}/P_{\mathrm{O}_2}^{1/4} \tag{23}$$

$$P_{\mathrm{NO}_2} = (K_E^{1/2}/K_F)\,P_{\mathrm{CO}_2}^{1/2}\,P_{\mathrm{O}_2}^{1/4} \tag{24}$$

$$P_{\mathrm{NO}_x} = K_E^{-1/2}\,[1 + (K_E/K_F)\,P_{\mathrm{O}_2}^{1/2}]\,P_{\mathrm{CO}_2}^{1/2}/P_{\mathrm{O}_2}^{1/4} \tag{25}$$

$$P_{\mathrm{NO}}/P_{\mathrm{NO}_x} = K_F/(K_F + K_E P_{\mathrm{O}_2}^{1/2}) \ . \tag{26}$$

Region 23. For the condition $P_{\mathrm{O}_2} > (P_{\mathrm{O}_2})_{\mathrm{e}}$ following equations are obtained

$$P_{\mathrm{NO}} = K_M^{-1/2}\, P_{\mathrm{CO}_2}^{1/2}/P_{\mathrm{O}_2}^{3/4} \tag{27}$$

$$P_{\mathrm{NO}_2} = K_N^{-1/2}\, P_{\mathrm{CO}_2}^{1/2}/P_{\mathrm{O}_2}^{1/4} \tag{28}$$

$$P_{\mathrm{NO}_x} = K_N^{-1/2}\, [(K_N/K_M)^{1/2}/P_{\mathrm{O}_2}^{1/2} + 1]\, P_{\mathrm{CO}_2}^{1/2}/P_{\mathrm{O}_2}^{1/4} \tag{29}$$

$$P_{\mathrm{NO}}/P_{\mathrm{NO}_x} = K_N^{1/2}/(K_N^{1/2} + K_M^{1/2} P_{\mathrm{O}_2}^{1/2}) \ . \tag{30}$$

The K_M and K_N in the equations from (*27*) to (*30*) are the equilibrium constants of the following reactions

$$\mathrm{CaCO_3 + 2\ NO + 3/2\ O_2 = Ca(NO_3)_2 + CO_2} \tag{M}$$

$$\mathrm{CaCO_3 + 2\ NO_2 + 1/2\ O_2 = Ca(NO_3)_2 + CO_2} \ , \tag{N}$$

where

$$(M) = 3\ (A) + 2\ (C) - 4\ (B) - (D) \tag{31}$$

$$(N) = (A) + 2\ (C) - 2\ (B) - (D) \ . \tag{32}$$

3. *The Hydroxide and the Carbonate are Coexistent*

We can describe the behavior of the system either by equations of the first case or by equations of the second case, together with an additional condition given by the equilibrium of the reaction (*D*), namely

$$P_{\mathrm{H_2O}}/P_{\mathrm{CO}_2} = K_D \ , \tag{33}$$

which express the simultaneous existence of the hydroxide and the carbonate in the system. Here again, we can distinguish among three regions of existence denoted as 31, 32 and 33, and for which the following relations are obtained.

Region 31. Here the partial pressure of oxygen is that of equilibrium one, and the partial pressures of nitrogen compounds are given by the equations

$$\mathrm{NO}:\ (5) + (33)\ \text{or}\ (19) + (33) \tag{34}$$

$$\mathrm{NO_2}:\ (6) + (33)\ \text{or}\ (20) + (33) \tag{35}$$

$$\mathrm{NO}_x:\ (7) + (33)\ \text{or}\ (21) + (33)\ \ . \tag{36}$$

Region 32. Here $P_{O_2} < (P_{O_2})_e$, and

$$\mathrm{NO}:\ (9) + (33)\ \text{or}\ (23) + (33) \tag{37}$$

$$\mathrm{NO_2}:\ (10) + (33)\ \text{or}\ (24) + (33) \tag{38}$$

$$\mathrm{NO}_x:\ (11) + (33)\ \text{or}\ (25) + (33)\ \ . \tag{39}$$

Region 33. Here $P_{O_2} > (P_{O_2})_e$, and

$$\mathrm{NO}:\ (15) + (33)\ \text{or}\ (27) + (33) \tag{40}$$

$$\mathrm{NO_2}:\ (16) + (33)\ \text{or}\ (28) + (33) \tag{41}$$

$$\mathrm{NO}_x:\ (17) + (33)\ \text{or}\ (29) + (33)\ \ . \tag{42}$$

For the fraction of nitrogen monoxide from both nitrogen oxides, no additional condition is needed, since in the pertaining equations the partial pressure of water vapor and of carbon dioxide do not appear, and the corresponding equations yield identical results both in the first and in the second case. Namely, we can write

$$(8) = (22) \tag{43}$$

$$(12) = (18) = (26) = (30)\ \ . \tag{44}$$

From the analysis of all the three cases given above, the following general conclusions can be drawn on the effect of water vapor, carbon dioxide, and oxygen on the partial pressure of nitrogen oxides.

In the first case the calcium hydroxide is present and the fugacity of both nitrogen oxides is increased with the square root of partial pressure of water vapor.

In the second case the calcium carbonate is present and the same dependence is found for the effect of carbon dioxide.

In the third case, where both the hydroxide and the carbonate are present, the above dependences remain of the same form with only one condition, that the partial pressure of water vapor and of carbon dioxide are connected through the equation (*33*).

The effect of oxygen depends both on the kind of nitrogen oxide and on the region of existence, however, these dependences are of the same form in all three cases considered above. The situation can be understood easily, if we take into consideration, that the chemical equations (*A*), (*B*), and (*C*) are isomorphic with the equations (*E*), (*F*), and (*G*). And the same isomorphy exists with the first three equations of the previous paper[1], where the effect of oxygen is treated in more details.

SPECIAL PART

We have calculated the equilibrium constants K_i of reactions (*A*) to (*G*), (*H*), (*K*), (*L*), (*M*) and (*N*) from a simplified equation of the form

$$\ln K_i = - H_i^0/\boldsymbol{R}T + S_i^0/\boldsymbol{R} \quad . \qquad (45)$$

Here H_i^0 and S_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 H_i^0 exceeds many times the deviation caused by neglecting the higher members. To calculate the values of H_i^0 and S_i^0 , the thermodynamic quantities were taken from the source[2]. To estimate the missing values of entropy and heat capacity of the calcium nitrite, we have extended the method proposed previously[3]. The values of H_i^0 and S_i^0 are given in Table I, and the calculated temperature dependences of equilibrium constants are represented in Fig. 1. The coordinates were selected so that the resulting dependences are linear. The equilibrium partial pressures of nitrogen oxides in all nine regions of existence were calculated, and typical results are graphicaly represented in Figs 2 – 9. In these figures, the area between the dotted straight lines *a* and *d* represents the range of possible practical application, i.e. the range between 10^{-1} and 10^{-4} volume percents of nitrogen oxides in the gas.

DISCUSSION

The case, where only the calcium hydroxide is present, is illustrated in Figs 2 – 5. If the partial pressure of oxygen is equal (Fig. 2) or lower (Fig. 3) than the equilibrium one, the calculated partial pressures of nitrogen oxides exceed the area between the dotted lines *a* and *d* at most temperatures. The practical use of the calcium hydroxide for removing the nitrogen oxides is here excluded. Only if the partial pressure of oxygen is higher than the equilibrium one (Fig. 4 and Fig. 5), the calculated partial pressures of nitrogen oxides are mostly lower than those given by lines *a* and *d*, and the application of the calcium hydroxide seems feasible, at least at lower temperatures.

A similar situation can be found in the second case, where only the calcium carbonate is present, as it is evident from Figs 6 – 9. At lower partial pressures of oxygen $P_{O_2} < (P_{O_2})_e$, the calculated partial pressures of nitrogen oxides are even much higher (Fig. 6 and Fig. 7). The eventual practical applicability appears to be less favorable than in the first case. Similarly, at higher partial pressures of oxygen $P_{O_2} > (P_{O_2})_e$, the practical use of the calcium carbonate may be faesible, as it is evident from Fig. 8 and Fig. 9, at least at lower temperatures.

In the third case, where both the calcium hydroxide and calcium carbonate are coexistent, similar conclusions can be drawn on the effects of temperature and of partial

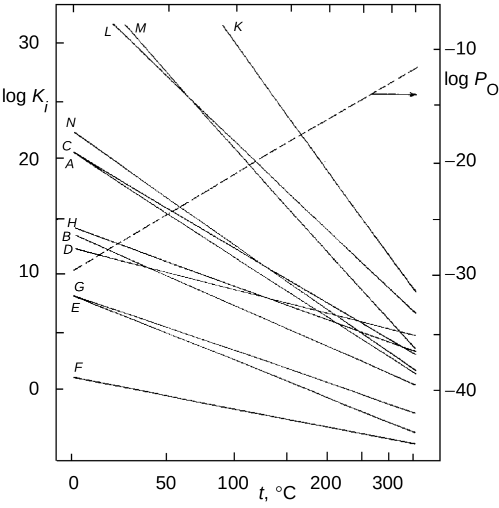

FIG. 1

Temperature dependence of equilibrium constants K_i of reactions (*A*) – (*H*) and of equilibrium partial pressure of oxygen P_{O_2} (dotted line)

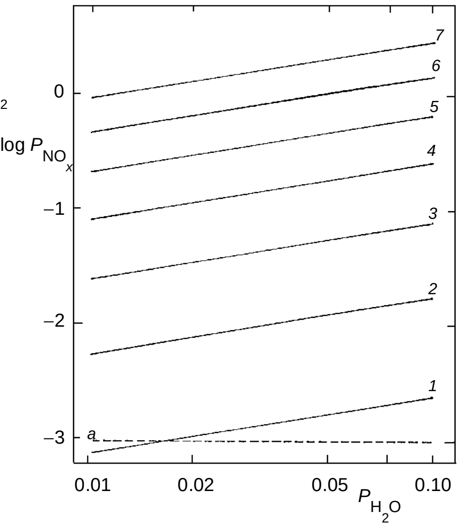

FIG. 2

Effect of water vapor and temperature on P_{NO_x} in Regions 11 and 31. Temperature in °C: *1* 50, *2* 100, *3* 150, *4* 200, *5* 250, *6* 300, *7* 350; the same notation is used in Figs 3, 4, and 5

TABLE I
Values of parameters in Eq. (*45*)

Reaction	$-H_i^0/2.303\,\boldsymbol{R}T$	$-S_i^0/2.303\,\boldsymbol{R}$
(*A*)	9 283.2	13.232
(*B*)	6 302.5	9.403
(*C*)	8 465.9	10.201
(*D*)	3 625.4	0.806
(*E*)	5 657.8	12.425
(*F*)	2 677.0	8.597
(*G*)	4 840.5	9.395
(*H*)	5 144.2	4.625
(*K*)	19 571.1	22.483
(*L*)	13 610.1	14.827
(*M*)	15 946.2	21.676
(*N*)	9 984.7	14.021

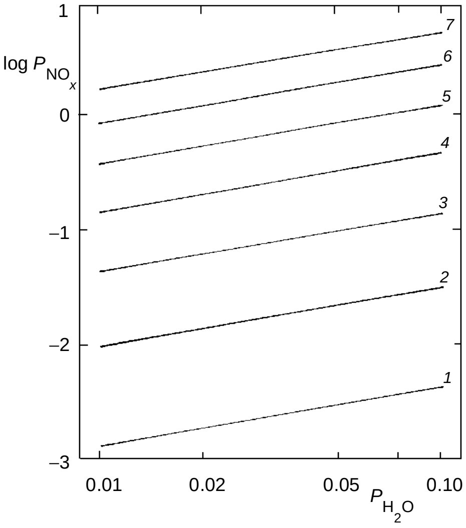

FIG. 3
Effect of water vapor and temperature on P_{NO_x} in Region 12 or 32. $P_{O_2} = (P_{O_2})_e/10$

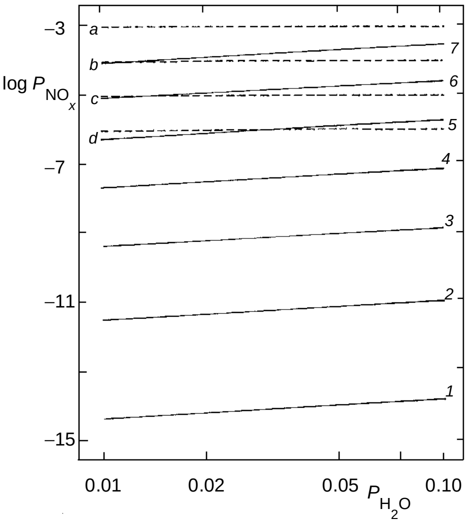

FIG. 4
Effect of P_{H_2O} and temperature on P_{NO_x} in Regions 13 and 33. $P_{O_2} = 0.05$

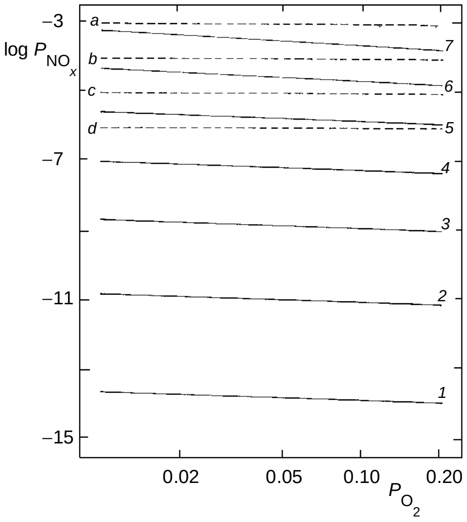

FIG. 5

Effect of oxygen and temperature on P_{NO_x} in Regions 13 and 33. $P_{H_2O} = 0.10$

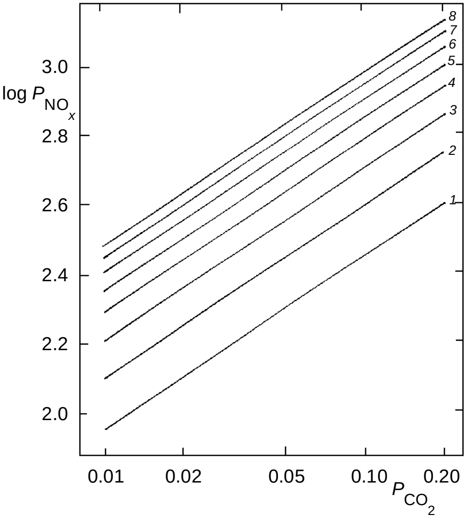

FIG. 6

Effect of carbon dioxide and temperature on P_{NO_x} in Regions 21 and 31. Temperature in °C: *1* 0, *2* 50, *3* 100, *4* 150, *5* 200, *6* 250, *7* 300, *8* 350; the same notation is used in Figs 7, 8 and 9

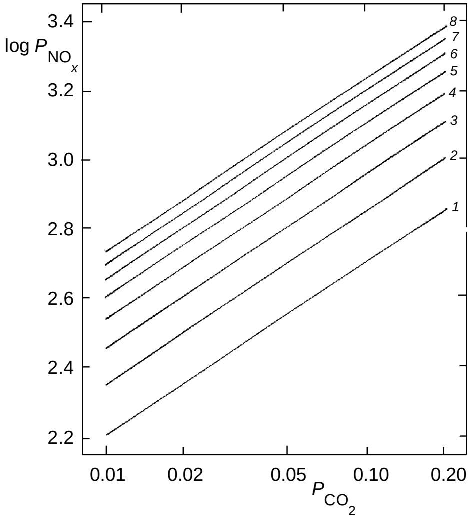

FIG. 7

Effect of carbon dioxide and temperature on P_{NO_x} in Regions 22 and 32. $P_{O_2} = (P_{O_2})_e/10$

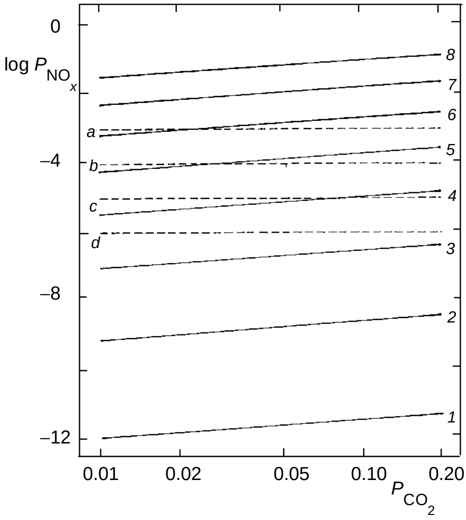

FIG. 8

Effect of carbon dioxide and temperature on P_{NO_x} in Region 23 or 33. $P_{O_2} = 0.05$

pressures of water vapor and of carbon dioxide, with only one exception, namely, that both the last named variables are connected by the equilibrium condition of the reaction (*D*). This condition proves to be restricting for practical applications, since the equilibrium constant K_D assumes values from 10^5 up to 10^{12} (Fig. 1) and the ratio of partial pressures of water vapor and of carbon dioxide under real conditions amounts from 1 up to 10^2; the first value corresponds roughly to waste gases and the second one atmospheric conditions. In addition, these values indicate, that under real conditions, the reaction (*D*) is completely shifted to the right hand side, and consequently, nor the first case, nor the third one can be taken into consideration for practical purposes. From what has been said, it follows, that even if the calcium hydroxide is used, it is transformed to the calcium carbonate, which can be used for removing the nitrogen oxides from waste gases under condition discussed above as the second case. For illustration, at temperatures up to 100 °C, the theoretical degree of nitrogen oxides removal exceeds 99% under common concentrations. All the conclusions given above are valid, if an equilibrium is reached in all the reactions considered.

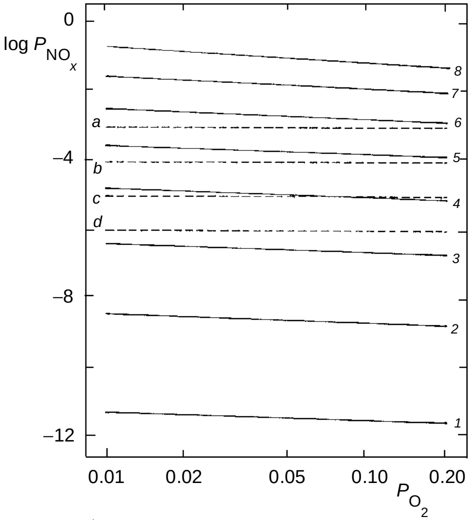

FIG. 9
Effect of oxygen and temperature on P_{NO_x} in Region 23 or 33. $P_{CO_2} = 0.10$

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