Sorption and Reactivity of Nitrous Oxide and Nitric Oxide in Crystalline and Amorphous Siliceous Sorbents.

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Calcium- and sodium-rich forms of chabazite and faujasite, mordenite and a synthetic zeolite with mordenite-like molecular-sieve properties, Vycor porous glass, a sodium aluminosilicate gel (Doucil), and a silica gel have been characterised as sorbents by using oxygen and argon as sorbates. These siliceous sorbents were then used in studies of the sorption of nitric oxide, and, in the case of chabazite, of nitrous oxide.

In chabazite nitrous oxide was stable up to 350°, in contrast to its behaviour when sorbed on certain oxides. Isosteric heats and excess entropies of the adsorbed gas decreased as v/v_m increased. In contrast to the stability of sorbed nitrous oxide, nitric oxide occluded by the crystalline zeolites underwent, usually with remarkable ease and nearly to completion (*e.g.*, in calcium- and sodium-rich faujasites and chabazites), a disproportionation reaction, $4NO = N_2O + N_2O_3$. In porous glass, sodium aluminosilicate gel, and silica gel sorption was less copious, and only in the first two sorbents at 0° was a limited disproportionation observed. There is thus a wide difference between the catalytic activity of the amorphous and the crystalline sorbents.

When nitric oxide was first sorbed in chabazite, porous glass, or the sodium aluminosilicate gel and then oxygen was also occluded, the nitric oxide remained wholly inactive to the oxygen. Occluded dinitrogen trioxide, formed by disproportionation of nitric oxide, liberated nitric oxide from chabazite at 150°, but the nitrogen dioxide also produced was tenaciously retained below 200°. The presence of intracrystalline NO_2^- and NO_3^- was also demonstrated, and ascribed to a side reaction with residual intracrystalline water ($N_2O_3 + H_2O = 2HNO_2$; $N_2O_4 + H_2O = HNO_2 + HNO_3$).

When charcoal was used as sorbent, nitric oxide underwent a different reaction, probably $4NO = N_2 + 2NO_2$.

MOLECULES sorbed in an intracrystalline environment may show unusual chemical reactivity. Hydrogen sulphide and ethylene sorbed in potassium benzenesulphonate form ethanethiol (Lange and Lewin, *Ber.*, 1930, **63**, 2156); in the same sorbent thiophen reacts with the sulphonate at 70° or above (Barrer, Drake, and Whittam, unpublished observation, see *Proc. Roy. Soc.*, 1953, **219** *A*, 32). Baba (*Bull. Chem. Soc. Japan*, 1930, **5**, 190) showed that carbon disulphide in chabazite turned the sorbent yellow and gave off hydrogen sulphide. He considered that this might be due to reaction between carbon disulphide and residual intracrystalline water. Following observations by Grandjean (*Bull. Soc. franç. Min.*, 1910, **33**, 5) and Wyart (*ibid.*, 1933, **56**, 81, 142), Barrer and Woodhead (*Trans. Faraday Soc.*, 1948, **44**, 1001) found that oxygen reacted with mercury sorbed in chabazite, giving a yellow tint to the chabazite. The sorbent turned black on exposure to moist air, and gave deep colours also with other electron-donor molecules (sulphur dioxide, ammonia, and hydrogen sulphide). It was suggested that an array of mercury and oxygen ions was formed interstitially and that mercury ions could further co-ordinate with the water or other molecules.

Zeolites can also exhibit dehydrohalogenating powers. Thus Barrer and Brook (*ibid.*, 1953, **49**, 940) found that sorption of trifluoro- or chlorodifluoro-methane in chabazite was an irreversible process in which the sorbent was attacked and gradually rendered amorphous and non-sorbing. Hydrothermal extraction of the product aggregated molecularly or ionically dispersed calcium fluoride, formed in the process, into identifiable fluorspar crystals. An initial interstitial liberation of hydrogen fluoride will explain these results. In another instance, hydrogen chloride was smoothly and easily removed from *tert.*-butyl chloride at room temperature, even though the organic molecule was itself too large to enter the crystals. The olefin formed then polymerised to give liquid oils (Barrer and Brook, *Trans. Faraday Soc.*, 1953, **49**, 940). With the secondary chloride, *iso*propyl chloride, which again could not penetrate the crystals, this removal of hydrogen chloride did not occur until about 200°, and even then was very slow; with chloroform, also too large to be occluded, no dehydrochlorination at all could be detected. The hydrogen chloride liberated from *tert.*-butyl chloride was occluded in large amount, and formed some interstitial calcium chloride together with the hydrogen-form of chabazite. No structural change of the lattice was however observed.

A different kind of intracrystalline reaction was noted by Barrer (*Nature*, 1949, **164**, 112), who found that ammonia could be burned away (as nitrogen and water) from the ammonium forms of chabazite and mordenite by oxygen occluded at about 330°. The products were crystalline hydrogen zeolites which, like the parent crystals, were excellent molecular-sieve sorbents (*idem, ibid.*, p. 112).

Considerable interest may therefore attach to reactions induced by or involving zeolites, especially where these processes occur in an intracrystalline environment. The present paper describes the sorption and reactivity of nitrous and nitric oxide in various siliceous sorbents, both crystalline and amorphous. The results add to knowledge of intracrystalline behaviour, especially as regards nitric oxide.

EXPERIMENTAL

Helium (used for dead-space determinations), argon, and oxygen were supplied pure by the British Oxygen Co. Ltd. Nitrous oxide, also obtained from this source, was condensed, and residual gases were pumped away; it was then fractionated, and the vapour density of the pure fraction determined by weighing (Found: 22·02. Calc.: 22·01). Nitric oxide was prepared by Chrétien and Longi's method (*Compt. rend.*, 1943, **217**, 504); it was then fractionated until the product had a satisfactory vapour density. The gas was prepared on two occasions, in 4-l. quantities. Vapour densities found were 14·98 and 14·95 (Calc. for NO: 15·00).

Gas-volumetric sorption methods (Barrer and Brook, *Trans. Faraday Soc.*, 1953, **49**, 940) were employed in the subsequent studies. The apparatus was designed to work in triplicate, there being three sorption bulbs each with associated gas burettes, Toepler pumps, pressure gauges, and gas-supply trains. *X*-Ray examination of some of the sorbents was carried out with a Hilger HRX *X*-ray unit and filtered Cu-K_α radiation. As low-temperature baths for the sorbent bulbs liquid nitrogen (−195°), liquid oxygen (−183°), solid carbon dioxide (−78°), melting chloroform (−63·5°), melting carbon tetrachloride (−22·5°), and ice (0°) were used. For higher temperatures, electrical heating of the sorbent was employed.

In quantitative analysis of binary gas mixtures, and in tests of purity of single gases, the determination of vapour density by direct weighing of gas samples at known pressures was extensively employed. This method was normally very satisfactory indeed for the systems studied.

All sorbents were outgassed for 24 hr. at the temperatures given in parentheses. The crystalline sorbents were chabazite (pink and white varieties) (450°), mordenite, faujasite (a synthetic specimen of composition $Na_2O,Al_2O_3,2{\cdot}6SiO_2,6{\cdot}2H_2O$, and made available by Linde Air Products Co.), a synthetic zeolite, Na–A (as its sodium-form, which exhibits molecular-sieve properties analogous to those of mordenite; also supplied by Linde Air Products Co.) (all 350°). These zeolites represent a group of molecular-sieve crystals in which the order of openness is sodium- and calcium-faujasite > calcium-chabazite > sodium-chabazite, mordenite, and synthetic zeolite (Na–A). Faujasite is so open in structure that it readily occludes *neo*pentane (Barrer, unpublished observation).

Sodium-rich chabazite was prepared from calcium-rich natural chabazite by successive treatments with concentrated aqueous sodium chloride and heating on a steam-bath. After three treatments no more calcium could be detected in the mother-liquor, and the crystals were thoroughly washed and stored for use. Calcium-rich faujasite was made in the same way from the synthetic sodium-form by use of aqueous calcium chloride.

Amorphous sorbents employed were porous glass (supplied by the Corning Glass Co., in the form of rod; the composition was approximately SiO_2, 96%; B_2O_3, 4% with very little Al_2O_3 and Na_2O). Sections of rod were ground, and the powder degassed (200°). "Doucil" sodium aluminosilicate water-softener was available commercially. It was ground to powder and outgassed (200°). Silica gel was supplied by B.D.H. Ltd., as employed for desiccation. The particle size was between 30 and 120 mesh. It was ground and outgassed (290°). An activated sorbent charcoal was also supplied by B.D.H. Ltd. and was likewise ground and outgassed (300°).

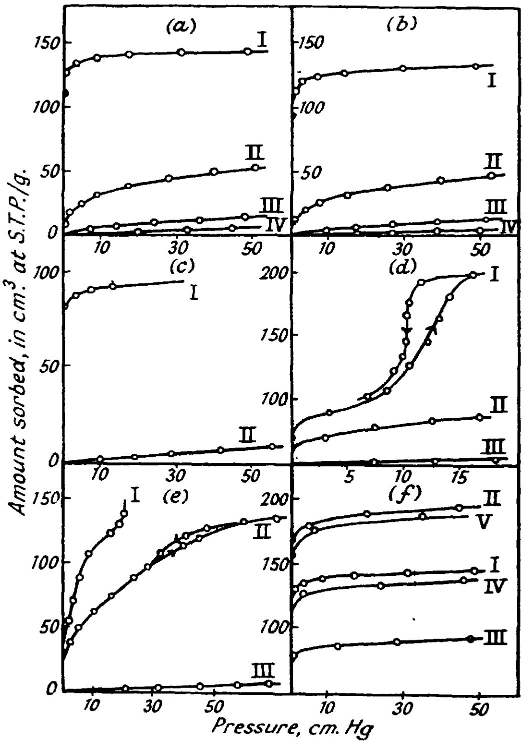

FIG. 1. *Characteristic isotherms in siliceous sorbents.*

(*a*) Oxygen in chabazite : (I), −183°; (II), −78°; (III), 0°; (IV), 50°.
(*b*) Argon in chabazite : (I), −183°; (II), −78°; (III), 0°; (IV), 50°.
(*c*) Oxygen in mordenite : (I), −183°; (II), 0°.
(*d*) Oxygen in porous glass : (I), −193·9°; (II), −183°; (III), −78°.
(*e*) Oxygen in Doucil aluminosilicate gel : (I), −194·4°; (II), −183°; (III), −78°.
(*f*) Curve (I), Oxygen at −183° in chabazite (Ca-rich); (II), Oxygen at −183° in Ca-faujasite; (III), Oxygen at −183° in Na-chabazite; (IV), Oxygen at −183° in synthetic zeolite ("Na–A"); V), Oxygen at −183° in Na-faujasite.

Characterisation of the Sorbents.—Before investigation of the sorption of nitrous and nitric oxide, the sorbents, some of which have previously been little studied (*e.g.*, faujasite, Na–A, and Doucil), were characterised and compared by a study of oxygen and argon sorption. Typical isotherms are shown in Fig. 1.

Faujasites (sodium- and calcium-forms) show saturation values for oxygen approaching 200 cm.³ (at S.T.P.)/g.; in calcium-chabazite and in Na–A this figure is about 150 cm.³. Sodium-rich chabazite and mordenite give saturation values approaching 100 cm.³. Saturation values for argon are rather less in all cases investigated. Evidently faujasite surpasses all the other zeolites not only in openness of the framework but also in the amount of interstitial volume available for sorption. Sorption at −78° was still substantial in chabazite and in faujasite, but at higher temperatures the sorption falls off rapidly. In all the crystalline zeolites the isotherms are of Type I in Brunauer's classification (" Physical Adsorption of Gases and Vapours," Oxford University Press, 1945, p. 150), a situation arising because in no case are the channels traversing the crystals, in which occlusion occurs, sufficiently wide for capillary condensate or multilayers to appear.

Interesting changes occur in the character of the isotherms in porous glass and in Doucil. Here, crystalline character has disappeared, capillaries are wider and, unlike those in zeolites, show a considerable range in sizes. As a result capillary condensate appears at higher relative pressures, with associated hysteresis loops and isotherms which are (for porous glass) or tend to be (for Doucil) of Type IV in Brunauer's classification. By applying Kelvin's equation to the desorption branch of the isotherms the pore-size distributions of Figs. 2*a* and 2*b* were obtained (Foster, *Discuss. Faraday Soc.*, 1948, **3**, 41). Porous glass gives a narrower distribution of sizes than does Doucil, but the maximum in the curve of d*v*/d*r* against *r* occurs at a larger value of *r* (~27 Å) for porous glass than for Doucil (~20 Å). In these calculations the thickness of the adsorbed layer remaining when the meniscus just disappears is taken into account (*idem, ibid.*; Barrer and Barrie, *Proc. Roy. Soc.*, 1952, **213**, *A*, 250).

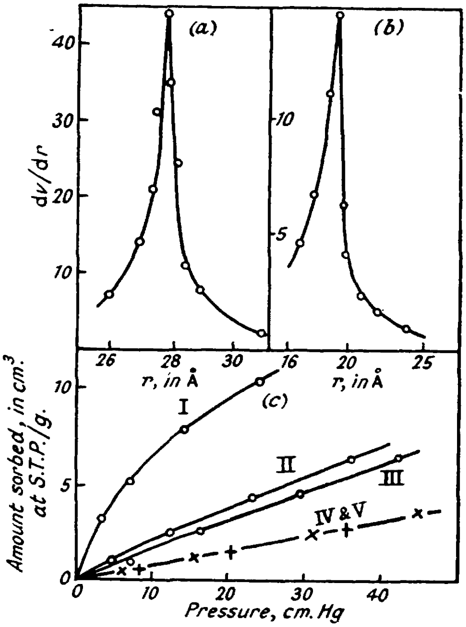

FIG. 2. *Pore-size distributions in* (*a*) *porous glass and* (*b*) *" Doucil " aluminosilicate gel.*

FIG. 2 (*c*). *Degree of selectivity shown between several zeolites and between* Ca- *and* Na-*forms of zeolite, in the sorption of oxygen at* 0°.

(I) and (II), a Ca- and a Na-chabazite respectively. (III) and (IV; points marked x), Ca- and Na-faujasites, respectively. (V), Synthetic zeolite " Na-A " (points marked +).

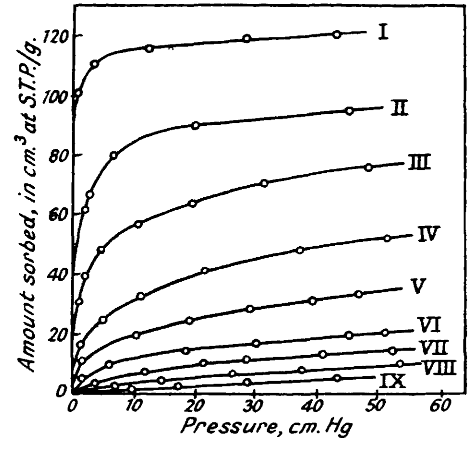

FIG. 3. *Sorption isotherms of nitrous oxide in chabazite in the range* −78° *to* 350°: (I), −78°; (II), 0°; (III), 50°; (IV), 100°; (V), 150°; (VI), 200°; (VII), 250°; (VIII), 300°; (IX), 350°

The affinity between oxygen and the sorbent varies according to the cation present. Fig. 2*c* shows that the affinity of oxygen is greater for the calcium- than for the sodium-form of faujasite and of chabazite (in the latter allowance is made for the different saturation values). These differences in affinity almost certainly arise from different heats of sorption among the cationic forms (Barrer, *Trans. Faraday Soc.*, 1944, **40**, 555; Barrer and Riley, *ibid.*, 1950, **46**, 853).

It is evident from the data presented that in the above sorbents, together with the B.D.H. silica gel, one has a diverse group of siliceous sorbents from the viewpoints both of chemical composition and of physical structure and porosity.

Sorption of Nitrous Oxide.—The nitrous oxide molecule (m. p. −90·9°; b. p. −88·5°; dipole moment, 0·17 D) is linear in form and has very similar physical properties to carbon dioxide. As would be expected from this, nitrous oxide was sorbed much more strongly than oxygen or argon, so sorption was investigated between −78° and 350° (Fig. 3).

At higher temperatures nitrous oxide can be decomposed catalytically into its elements (Dell, Stone, and Tilley, *ibid.*, 1953, **49**, 201; Amphlett, *ibid.*, 1954, **50**, 273). However, no such decomposition occurred in chabazite up to 350°, since the high-temperature isotherms were reversible. Moreover, the desorbed gas was retained after each sorption isotherm and the vapour density was measured and shown to be that of nitrous oxide. The rate of sorption varied with temperature: not more than 10 min. was needed per isotherm point at 350°, but at least 3—4 days were needed at −78°. Because of slowness of sorption at lower temperatures, isotherms at −78°, and possibly at 0° and 50°, may not correspond to full equilibration.

Thermodynamic Considerations.—Isosteric heats of sorption of nitrous oxide, and for comparison those of oxygen, were determined in chabazite as a function of the amounts sorbed. These heats, obtained from smoothed isosteres, are shown in Table 1 and Fig. 4*c*. As noted in the previous section, there may be an error in ΔH for nitrous oxide in Table 1, cols. 6 and 7, owing to the slow rate of equilibration at the lowest temperatures. Another factor of importance is temperature control, which in the high-temperature furnaces was accurate to ±1°, giving a maximum variation of 4% for the temperature interval of 50° in Table 1.

TABLE 1. *Isosteric heats of sorption of* N_2O *in chabazite.*

v (cm.³ at S.T.P./g.)	ΔH (cal./mole) over range *						
	1	2	3	4	5	6	7
1	15,260	15,410	15,280	—	—	—	—
2	15,130	15,230	14,940	—	—	—	—
3	15,000	15,090	14,870	—	—	—	—
4	14,670	14,920	14,740	—	—	—	—
5	14,540	14,330	14,440	—	—	—	—
6	14,210	14,030	13,860	—	—	—	—
7	14,030	13,750	13,270	—	—	—	—
8	—	13,490	12,610	—	—	—	—
9	—	13,220	11,930	—	—	—	—
10	—	12,970	11,460	11,620	—	—	—
11	—	—	10,980	11,570	—	—	—
12	—	—	10,700	11,520	—	—	—
15	—	—	—	11,370	11,250	—	—
18	—	—	—	11,180	10,080	—	—
20	—	—	—	11,080	9,540	—	—
22	—	—	—	11,040	9,490	—	—
25	—	—	—	—	9,300	—	—
28	—	—	—	—	9,240	—	—
30	—	—	—	—	9,270	11,090	—
32	—	—	—	—	9,100	11,000	—
35	—	—	—	—	9,220	10,970	—
38	—	—	—	—	9,410	10,950	—
40	—	—	—	—	—	10,640	—
42	—	—	—	—	—	10,240	—
45	—	—	—	—	—	10,210	—
48	—	—	—	—	—	10,180	—
50	—	—	—	—	—	10,150	9850
52	—	—	—	—	—	9,890	9520
55	—	—	—	—	—	9,860	9310
60	—	—	—	—	—	—	9220

* Where the temperature ranges for which these values are quoted are as follows: (1) 300—350°, (2) 250—300°, (3) 200—250°, (4) 150—200°, (5) 100—150°, (6) 50—100°, (7) 0—50°.

The main interests of the data were the high heat of sorption of nitrous oxide, and the way in which ΔH for both gases decreased at first rapidly and then very slowly as the charge of sorbate rises. The initial change in the isosteric heat with amount sorbed outweighs any temperature coefficient in ΔH. The partial molar entropies of the sorbed nitrous oxide were determined as functions of the amount, only the isotherms between 200° and 350° being used, for ΔH in Table 1 is most consistent at this high-temperature end of the measurements.

The standard state of the gas was taken as 1 atm. At 298° K the standard entropy S^{+G} of nitrous oxide is 51·44 e.u. (Blue and Giauque, *J. Amer. Chem. Soc.*, **1935**, **57**, 991), and from Kassel's heat-capacity data (*ibid.*, **1934**, **56**, 1838) the standard entropy at any other temperature was determined by graphical integration ($S^{+G}_2 - S^{+G}_1 = 2{\cdot}303 \int_{T_1}^{T_2} C_p \, d \ln T$). For the isothermal transfer of a mole of gaseous sorbate from the gas phase to an infinite amount of the sorbent–sorbate system over which the equilibrium pressure is p_Γ and the sorbate concentration Γ one has :

$$\Delta\mu^+_\Gamma = \overline{\Delta H}{}^+_\Gamma - T\overline{\Delta S}{}^+_\Gamma = \boldsymbol{R}T \ln p_\Gamma \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $\Delta\mu^+_\Gamma = \mu^\sigma_\Gamma - \mu^{+G}$ is the difference in the chemical potential of sorbate in the standard state in the gaseous phase (μ^{+G}) and the chemical potential of sorbate at concentration Γ in or on the sorbent. Similarly $\overline{\Delta H}{}^+_\Gamma = \overline{H}{}^\sigma_\Gamma - H^{+G}$ is the isosteric heat of sorption, given by $\overline{\Delta H}{}^+_\Gamma = \boldsymbol{R}T^2 \, \partial \ln p_\Gamma / \partial T$ (ΔH in Table 1). Finally, $\overline{\Delta S}{}^+_\Gamma = \overline{S}{}^\sigma_\Gamma - S^{+G}$ is the differential molar entropy of transfer of sorbate from gas phase to an infinite amount of sorbent–sorbate system in which sorbate has a concentration Γ. $\overline{H}{}^\sigma_\Gamma$ and $\overline{S}{}^\sigma_\Gamma$ are the partial molar heat and entropy of sorbate in or on the sorbent and H^{+G} and S^{+G} are the standard heat content and entropy of the gaseous sorbate. In the nomenclature, we have followed the symbols used by Everett (*Trans. Faraday Soc.*, **1950**, **46**, 453, 942, 957).

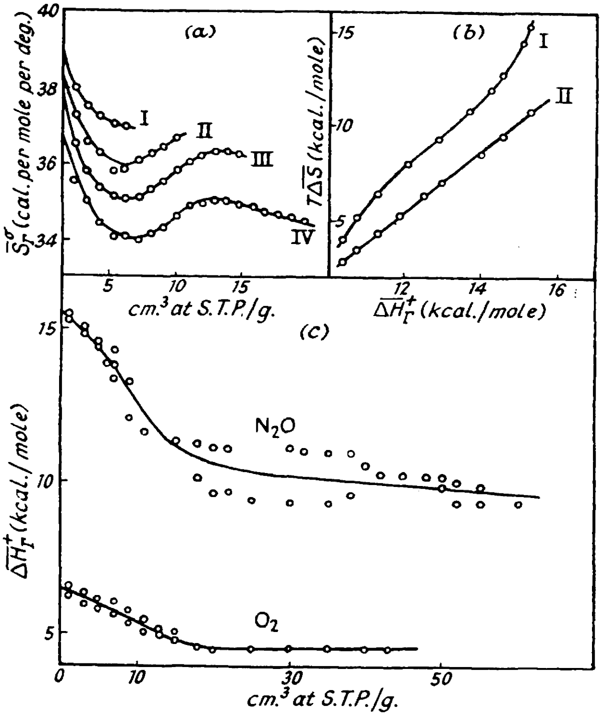

FIG. 4. (*a*) *Partial molar entropy of nitrous oxide, occluded by chabazite, as a function of temperature and of amount sorbed* : (I), 350°; (II), 300°; (III), 250°; (IV), 200°.

(*b*) *The relations between the excess entropy of sorption,* $\overline{\Delta S}{}^*_\Gamma$ (*Curve I*), *and the standard differential entropy of sorption,* $\overline{\Delta S}{}^+_\Gamma$ (*Curve II*), *and the isosteric sorption heat,* $\overline{\Delta H}{}^+_\Gamma$.

(*c*) *The relation between* $\overline{\Delta H}{}^+_\Gamma$ *and amount sorbed for nitrous oxide and for oxygen in chabazite.*

From equation 1 we obtain :

$$\overline{S}{}^\sigma_\Gamma = S^{+G} + (\overline{\Delta H}{}^+_\Gamma/T) - \boldsymbol{R} \ln p_\Gamma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Since all the terms on the right-hand side of equation (2) are available, $\overline{S}{}^\sigma_\Gamma$ can be derived. These partial molar entropies of the sorbed nitrous oxide are shown in Fig. 4*a* as a function of the volume V sorbed (in c.c. at S.T.P./g.). The values of $\overline{S}{}^\sigma_\Gamma$ are substantial and increase, as might be expected, with rising temperature. The presence of minima is interesting, but in view of the large values of $\overline{S}{}^\sigma_\Gamma$ and of possible limitations in their accuracy any significance of the relatively shallow minima should not be emphasised.

According to the model for localised Langmuir sorption, the differential configurational entropy $\bar{S}^{\sigma,l}{}_{\Gamma} = -\boldsymbol{R}\ln\theta/(1-\theta)$. By subtracting this quantity from $\Delta S^{+}{}_{\Gamma}$, obtained from equation (1), $\overline{\Delta S}^{*}{}_{\Gamma}$, the excess differential molar entropy of sorption, may be obtained. This entropy is associated directly with the loss of mobility when the gas is transferred from the gas phase to the sorbed phase. When $T\overline{\Delta S}^{*}{}_{\Gamma}$ is plotted against $\Delta H^{+}{}_{\Gamma}$, the graph is nearly linear (Fig. 4*b*). A similar relation was observed in the adsorption of a number of substances on charcoal (Everett, *loc. cit.*, p. 959), and was there regarded as compatible with a localised sorption in which there were departures from the ideal Langmuir model due to a simultaneous variation of both heat and entropy of sorption. In the calculations of Fig. 4*b*, V_m was taken as 130 cm.³ at S.T.P./g., and the standard state in the gas phase was 1 mm. pressure.

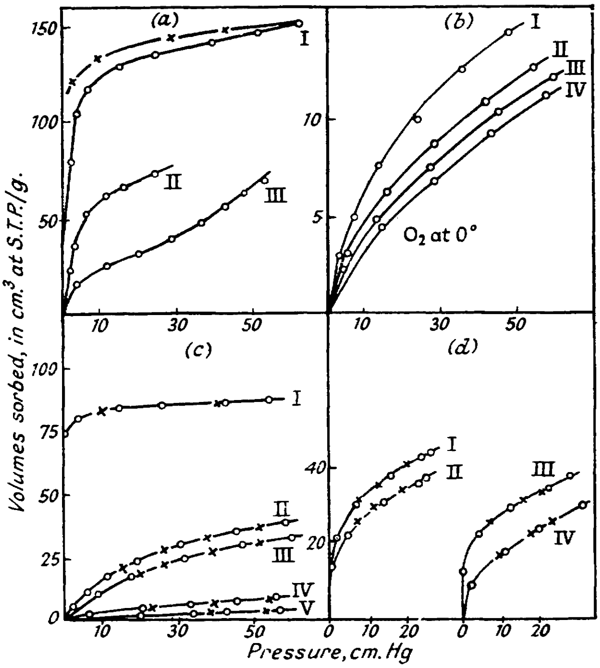

FIG. 5. (*a*) *Sorption of* NO *in chabazite and mordenite.*

—○—, Adsorption points.
—×—, Desorption points.

(I) Chabazite at 0°; (II) mordenite at 0°; (III) chabazite at 100°.

(*b*) *Decrease in sorption of oxygen by chabazite at* 0° *after prior sorption of nitric oxide followed by thorough outgassing.*

(I), Oxygen uptake on fresh sorbent; (II), oxygen uptake after one treatment with nitric oxide; (III), oxygen uptake after two treatments with nitric oxide; (IV), oxygen uptake after three treatments with nitric oxide.

(*c*) *Sorption of oxygen and argon by chabazite after first sorbing the quantities of nitric oxide given in parentheses.*

—○—, Adsorption points.
—×—, Desorption points.

(I), O_2 at −183° (46·0); (II), O_2 at −78° (19·74); (III), A at −78° (19·74); (IV), O_2 at 0° (14·80); (V), O_2 at 50° (9·79).

(*d*) *Sorption of oxygen and argon in porous glass (Curves I and III respectively), and in porous glass after first sorbing* 19·49 *cm.³ at S.T.P./g. of nitric oxide (Curves II and IV respectively).*

All isotherms are at −183°.

—○—, Adsorption points.
—×—, Desorption points.

Similar calculations were made for oxygen at −63·5°, assuming V_m = 150 cm.³ at S.T.P./g. Here for $\theta > 0{\cdot}1$, $\overline{\Delta H}^{+}{}_{\Gamma}$ and $T\overline{\Delta S}^{*}{}_{\Gamma}$ were nearly constant. Even for $\theta < 0{\cdot}1$, plots of $\overline{\Delta H}^{+}{}_{\Gamma}$ and $T\overline{\Delta S}^{*}{}_{\Gamma}$ against the amount sorbed followed parallel courses.

That a linear correlation between $\overline{\Delta H}^{+}{}_{\Gamma}$ and $T\overline{\Delta S}^{*}{}_{\Gamma}$ can best be interpreted as a localised sorption does not seem wholly convincing. However, localised sorption will always tend to be favoured when the heat of sorption decreases as θ increases, because the site heterogeneity will lead to anchoring of molecules to the most energetically sorbing sites.

Sorption of Nitric Oxide.—The sorption of nitric oxide (m. p. −163·7°; b. p. −151·8°; dipole moment 0·17 D) was first studied on chabazite at 0° and 100° and on mordenite at 0° (Fig. 5*a*). Sorption was clearly abnormal: a very large amount of nitric oxide was occluded for a gas of the above physical properties at the experimental temperatures; the sorption showed a slow drift and was irreversible as indicated by the desorption points in chabazite at 0° (Fig. 5*a*). The gas from this isotherm was then desorbed and collected in five fractions by freezing at −183°. The first fraction consisted of the gas present in the gas phase. With the exception of about 20%, the second fraction consisted of products desorbed directly from the chabazite, while for the other fractions the desorbate all came substantially from the chabazite. The fourth and the fifth desorption required heating of the sorbent to 100°. Vapour densities of the fractions then were: Fraction (1) 17·51; (2) 19·04; (3) 20·32; (4) 17·91; (5) 18·02. Thus the desorbate contains a gas or gases heavier than nitric oxide (vapour density, 15·00) and, from the variable vapour density, is a mixture of changing composition.

Each fraction was colourless and had a vapour pressure close to 2·7 mm. at −183°, *i.e.*, that of pure nitric oxide, thus indicating the presence of that gas. When air was admitted to each fraction, after completion of vapour-density measurements, the formation of brown nitrogen dioxide was observed.

From consideration of the starting material and of the above behaviour, the gas or gases in admixture with nitric oxide must (1) contain only the elements oxygen and nitrogen; (2) be of substantially higher molecular weight than nitric oxide; (3) have negligible vapour pressure at −183°; and (4) be colourless whether solid or gas. Only nitrous oxide fulfils these conditions, and the desorbate must be a binary mixture of this with nitric oxide. The presence of nitrous oxide was established by oxidising all the nitric oxide to nitrogen dioxide with excess of air, freezing at −183°, pumping away incondensibles (nitrogen and excess of oxygen), and fractionating the condensate at −78°. At this temperature the presumed nitrous oxide evaporated but not the nitrogen dioxide. The former was freed from any traces of the latter by contact with potassium hydroxide pellets, and the vapour density of the colourless gas was then measured and shown to be 22·02 (Calc. for N_2O : 22·01%).

Since nitrous oxide cannot for reasons of material balance be the sole decomposition product from nitric oxide, a higher oxide was thought to remain occluded in chabazite even at 100°. A sixth fraction was then desorbed, and collected at −183°, by raising the temperature of the chabazite progressively to 400°. This desorbate was a brown gas condensing to a blue liquid and finally to a blue solid. The gas attacked mercury (cf. nitrogen dioxide or dinitrogen trioxide) making accurate pressure and so density measurements difficult. However, at room temperature a vapour density of 35·8 ± 0·3 indicated that the gas contained nitric oxide. The existence of the two equilibria $N_2O_3 \rightleftharpoons NO + NO_2$ and $N_2O_4 \rightleftharpoons 2NO_2$ prevents further analysis, but the vapour density of $N_2O_4 \rightleftharpoons 2NO_2$ is *ca.* 42·6 at room temperature.

The above evidence then shows that nitric oxide in chabazite undergoes disproportionations such as

$$4NO = N_2O + N_2O_3 \qquad (1)$$

and

$$3NO = N_2O + NO_2 \qquad (2)$$

It was further demonstrated in a blank experiment that merely condensing nitric oxide for 100 hr. at −183° brought about no detectable disproportionation. Finally, it was established by the above procedures that the gas desorbed from chabazite after sorption at 100° and from mordenite after sorption at 0° had also undergone a partial disproportionation.

Disproportionation of Nitric Oxide by Other Siliceous Sorbents and by Charcoal.—The methods developed for chabazite were next applied to porous glass, silica gel, Doucil sodium aluminosilicate gel, and charcoal. The sorption by the three siliceous sorbents at 0° was much less than that in chabazite or mordenite. After 14 days at 0° the vapour density of the desorbate from porous glass was only 15·41, indicating a limited disproportionation. Also, some nitrogen dioxide was desorbed from the porous glass by heating it to 200°. A sorption period of 1 month at 0° (with daily 5-min. intervals at −183° to sorb all gases and help promote reaction) gave little further change, the vapour density being 15·47, while a 5-min. sorption time at −63·5° led to a desorbate of vapour density 15·39. These results show only slight disproportionation and suggest that the products thereof may inhibit further reaction by preferential occupation of the catalytically active centres. With silica gel after 10 days at 0° the desorbate had a vapour density of only 15·11, indicating negligible reaction of the sorbed nitric oxide. Doucil sodium aluminosilicate gel behaved like porous glass; 14 days' sorption at 0° followed by desorption gave a desorbate of vapour density 15·42, and nitrogen dioxide was also liberated when the gel was heated to complete desorption. When the nitric oxide was sorbed on either porous glass or Doucil at −183° and held for long periods at this temperature (~5 weeks) the desorbate had the vapour density of pure nitric oxide, so no detectable reaction had occurred.

It is thus clear that the three amorphous gel sorbents behave similarly in giving only limited or negligible disproportionation of sorbed nitric oxide, in contrast with the extensive disproportionation in chabazite and, as will be shown in the next section, in several other zeolites.

The behaviour of nitric oxide sorbed in charcoal was, however, quite distinct. Charcoal sorbed nitric oxide copiously (*e.g.*, 80 cm.^{3} at S.T.P./g. at 0° and 54 cm. Hg). A slow pressure drift suggested that an irreversible process was involved, and much of the desorbate was incondensable at −183° The desorbate had a vapour density of 14·78, and when this desorbate was partially condensed overnight at −183°, and the incondensable gas pumped away, the residue on evaporation yielded a colourless gas of vapour density 15·10. Since this gas also formed brown fumes on exposure to air it was clearly unchanged nitric oxide containing no nitrous oxide. The original lighter and incondensable constituent could only be nitrogen or carbon monoxide (vapour density 14·01). When the charcoal was heated to complete desorption much nitrogen dioxide was evolved. It was therefore considered that in part the nitric oxide was sorbed by charcoal to undergo the disproportionations $4NO = N_2 + 2NO_2$ or $6NO = N_2 + 2N_2O_3$. This behaviour is in agreement with Shah's observations (*J.*, 1929, 2661) but since it differed from the behaviour noted with the siliceous sorbents it was not studied further.

The Extent of Disproportionation of Nitric Oxide Sorbed by Zeolites.—Desorption by freezing the desorbate at −183° with the temperature of the sorbent not above 150° liberated only nitric and nitrous oxide from chabazite and other zeolites. Nitrogen dioxide was not evolved until temperatures of 200° or above were reached. By admitting a measured amount of nitric oxide to the sorbent, followed by desorption below 150°, one may then collect the nitric and nitrous oxide and analyse the binary mixture quantitatively through measurement of gas volumes and vapour-density.

The two possible reaction equations (1) and (2) were differentiated in the case of desorbate from chabazite following sorption of nitric oxide at −183°. On no occasion was an amount of nitrous oxide obtained more than one-quarter of the initial amount of nitric oxide sorbed and usually this amount of nitrous oxide was nearly exactly one-quarter of the initial charge of nitric oxide (cf. Table 2). It thus appeared that reaction (1) was operative and the percentage decompositions of nitric oxide given in Tables 2, 3, and 4 are all calculated on this assumption. It remains possible that at suitably high temperatures reaction (2) may begir to dominate.

In Table 2 are summarised the results of the analyses of the desorbate from chabazite following occlusion of the nitric oxide at −183°. Evidently reaction is virtually complete however short the time of contact between nitric oxide and chabazite at −183° and over a wide range in the amount of nitric oxide sorbed.

TABLE 2. *Extent of reaction* $4NO = N_2O + N_2O_3$ *in chabazite following sorption of* NO *at* −183°.

No. of run	Time at −183° (hr.)	Dose of NO sorbed (cm.³ at S.T.P./g.)	Vol. of N_2O recovered (cm.³ at S.T.P./g.)	Decompn. of NO, %	No. of run	Time at −183° (hr.)	Dose of NO sorbed (cm.³ at S.T.P./g.)	Vol. of N_2O recovered (cm.³ at S.T.P./g.)	Decompn. of NO, %
1	1/60	49·63	12·14	97·8	5	24	17·06	4·19	98·2
2	24	47·83	11·76	98·3	6	24	93·44	23·32	99·8
3	168	48·86	12·06	98·8	7	24	95·90	23·68	98·8
4	336	50·05	12·35	98·7					

TABLE 3. *Effect of temperature on the reaction* $4NO = N_2O + N_2O_3$ *in chabazite.*

No. of run	Temp.	Time (hr.)	Dose of NO sorbed (cm.³ at S.T.P./g.)	Vol. of N_2O recovered (cm.³ at S.T.P./g.)	Decompn. of NO, %
8	0°	1	16·03	3·18	79·3
9	0	7	14·51	2·91	80·2
10	0	24	16·35	3·16	77·3
11	0	25	16·74	3·31	79·1
12	0	119	14·45	2·91	80·6
13	0	1	10·35	2·01	77·7
14	−22·5	1	24·11	5·29	87·8
15	−63·5	1	24·10	5·70	94·6
16	−78	1	34·48	8·47	98·3
17	−78	31	54·98	13·78	100·2

The effect of the third variable, temperature, upon the extent of decomposition according to equation (1) is shown in Table 3, in which are summarised data for sorption temperatures of nitric oxide of −78°, −63·5°, −22·5°, and 0°. At −78° decomposition is as complete as when sorption occurs at −183°, but the proportion of nitric oxide disproportionated, though always high, is reduced especially at −22·5° and 0°. Runs 8—13 again show that times of contact of nitric oxide with chabazite at 0° of 1—119 hr. have no influence on the extent of reaction.

In the various runs reaction may not occur at the sorption temperature but during heating of the sorbent before desorption. From Table 3 one sees that reaction begins to be incomplete when the nitric oxide is initially sorbed at −63·5° or above, and it is thus probable when sorption was initially at −78° or −183° that the actual disproportionation of nitric oxide must have occurred below −63·5°.

Information regarding the disproportionation reaction follows also from a detailed consideration of a typical run, *e.g.*, run 2, Table 2. From 47·83 cm.^{3} of nitric oxide equation (1) requires 11·96 cm.^{3} of nitrous oxide, in close agreement with 11·76 cm.^{3} (all at S.T.P.) actually obtained. But the desorptions at 150°, although reaction according to equation (1) was complete and so all the nitric oxide was used up, always gave some nitric oxide in the desorbate. This apparent contradiction is due to the dissociation at 150° of sorbed dinitrogen trioxide: $N_2O_3 = NO + NO_2$. The nitric oxide is liberated but the dioxide is still sorbed. The maximum yield of nitric oxide by dissociation of the trioxide would in run 2, Table 2, be 11·96 cm.^{3}, compared with an actual recovery of 9·57 cm.^{3}.

Because chabazite was so much more effective in catalysing reaction (1) than the amorphous siliceous sorbents (porous glass, Doucil, silica gel), the reaction was studied in other crystalline zeolites in which either the cation was changed ($Na \rightleftharpoons Ca$) or the openness of the aluminosilicate framework was altered, or both. Thus the order of openness among the zeolites studied, based on molecular sieve experiments, was: Na-faujasite, Ca-faujasite > Ca-rich chabazite > Na-rich chabazite, and Na–A. Disproportionation was studied after sorption at 0°, by the procedures used with chabazite. The results given in Table 4 show that all the crystalline zeolites were very effective, the least effective being the less open structure Na–A. Mordenite was also effective in bringing about the reaction (1), but a breakage prevented quantitative results from being obtained.

TABLE 4. *Extent of the reaction* $4NO = N_2O_3 + N_2O$ *following sorption of* NO *at* 0° *in various zeolites.*

Sorbent	Vol. of NO sorbed (cm.^{3} at S.T.P./g.)	Vol. of N_2O recovered (cm.^{3} at S.T.P./g.)	Reaction, %
Ca-Faujasite	21·45	4·82	89·7
Na-Faujasite	22·50	4·08	72·8—83·6 *
Ca-rich Chabazite	(See Table 3)		79·6
Na-Chabazite	15·68	3·52	89·8—92·7 *
Na–A	16·31	1·07	26·2—42·7 *

* The nitric oxide was not in these cases wholly sorbed. Thus it was uncertain whether the nitrous oxide was produced by decomposition of the entire volume of nitric oxide used or only of that sorbed. Hence figures based on each possibility are given.

Formation of Intracrystalline Nitrite and Nitrate.—After chabazite used in sorbing nitric oxide had been thoroughly outgassed, the sorption of oxygen at 0° was re-determined, and found to be less than in the original crystals. Successive sorptions of nitric oxide each followed by desorption progressively reduced the subsequent sorption of oxygen (Fig. 5*b*). In all these runs the nitric oxide had been admitted at one or more of the temperatures −183°, −78°, 0°, and 50°. In a second series of experiments nitric oxide was sorbed three times at 250°, the sorbent being outgassed after each sorption and the oxygen uptake at 0° measured. The sorptive capacity of the chabazite towards oxygen was now even more drastically reduced.

Chabazite crystals showing this impaired sorptive capacity still gave the unaltered *X*-ray powder pattern of the original crystals. A sample of chabazite used in the sorption of nitric oxide at 0° was then outgassed for more than 60 hr. at 400—450° to ensure that all oxides of nitrogen would be removed. The sample was then hydrothermally extracted at 170° three times for several days. The extracts evaporated to dryness yielded solids totalling 2·1% by weight of the sample. Another similar experiment, on a different specimen of chabazite, gave a value of 2·4%. The solids were found to contain sodium, calcium, nitrite, and nitrate ions. The data are compatible with the view that dinitrogen trioxide (or nitrogen dioxide) produced by disproportionation of nitric oxide reacts with any residual intracrystalline water either at the sorption temperature or during outgassing: $H_2O + 2NO_2 = HNO_2 + HNO_3$; $H_2O + N_2O_3 = 2HNO_2$. The nitrous and nitric acid then form sodium and calcium nitrite and nitrate by reaction with interstitial cations, and convert the chabazite in part into its hydrogen form. The intracrystalline nitrate and nitrite are then responsible for the impaired sorptive powers of the chabazite.

When the hydrothermally extracted chabazite crystals were re-examined as sorbents they were found to be fully restored as compared with the original crystals (cf. Table 5). Since it has been shown that crystalline hydrogen chabazite is an excellent sorbent, quite equal to chabazite (Barrer, *Nature*, 1949, **164**, 112), the recovery shown in Table 5 is as expected for crystals which may be partly H-chabazite but from which occluded nitrite and nitrate have been removed.

TABLE 5. *Sorption of oxygen in original chabazite and in used and extracted chabazite, at* 76 *cm.*

	O_2 sorbed (cm.^{3} at S.T.P./g.) in :		
Sorption temp.	unused crystals	used and extracted crystals *	Increase in O_2 sorption, %
−183°	147·2	145·6	−1·09
−78	59·2	62·4	5·4
0	18·06	19·16	6·1
50	8·88	10·53	15·7
100	3·95	4·62	17·0

* Before extraction but after use in sorption of nitric oxide these crystals sorbed only 12·3 cm.^{3} at S.T.P. of oxygen at 0° and 76 cm.

Reactivity of Sorbed Nitric Oxide towards Oxygen.—At temperatures where oxygen and argon are rather weakly sorbed (*e.g.*, between −78° and 0°), nitric oxide is occluded by chabazite in considerable quantity without giving any measurable gas pressure. Thus sorption of oxygen and of argon can be quantitatively studied in crystals of chabazite suitably charged with nitric oxide. The reaction between gaseous nitric oxide and oxygen proceeds freely and can be measured down to −192° (Briner, Pfeiffer, and Malet, *J. Chim. phys.*, 1924, **21**, 25), and it was therefore of interest to study the reactivity of sorbed nitric oxide towards oxygen. Disproportionation of sorbed nitric oxide is a complicating factor and it depends on how rapidly and completely this reaction proceeds whether any sorbed nitric oxide is present to undergo oxidation. If some sorbed nitric oxide is present the nature of the sorption can still modify its reactivity, for chemisorption may remove the free-radical character of nitric oxide.

Doses of nitric oxide were admitted to the chabazite in quantity such that no measurable gas pressure developed. This eliminates the possibility of the gas-phase reaction $2NO + O_2 = 2NO_2$. Sorption of oxygen was then investigated; the oxygen was next pumped off without raising the temperature so that no oxide of nitrogen was displaced; and finally the sorption of argon was measured. Typical oxygen and argon isotherms are shown in Fig. 5*c* when the quantities of nitric oxide sorbed at each temperature were those given in Table 6. This table compares the amount of oxygen and of argon sorbed in presence and in absence of occluded nitric oxide at 76 cm. pressure, at various temperatures and for different amounts of sorbed nitric oxide. The sorptions of oxygen and of argon are reduced by occlusion of nitric oxide in practically the same ratios. Thus there is no evidence of any reaction between oxygen and sorbed nitric oxide. Further convincing evidence of lack of reactivity is afforded by the complete reversibility of the isotherms of oxygen in NO-chabazite. One may conclude either that sorbed nitric oxide has lost its free-radical character or that it has disproportionated completely ($4NO = N_2O + N_2O_3$).

TABLE 6. *Occlusion of oxygen and argon at* 76 cm. *in* NO-*chabazite.**

Temp. of isotherm	−183°	−78°	0°	50°
Vol. of NO sorbed	46·00	19·74	14·80	9·79
Vol. of O_2 sorbed	86·7	41·1	10·4	4·4
Vol. of O_2 sorbed in absence of NO	147·2	59·2	18·1	8·9
Vol. of A sorbed	—	34·8	9·4	—
Vol. of A sorbed in absence of sorbed NO	—	51·9	16·2	—
Decrease in O_2 sorption, %	41·1	30·6	41·3	50·6
Decrease in A sorption, %	—	32·9	42·4	—

* All volumes are in terms of cm.^{3} (at S.T.P.)/g.

Since porous glass and Doucil are relatively ineffective in disproportionating sorbed nitric oxide, the nitric oxide being desorbed largely unchanged, the procedures used with chabazite to study reactivity of sorbed nitric oxide towards oxygen were extended to these two gels. Essential results are summarised in Table 7. These show that the uptake of nitric oxide again reduces oxygen and argon sorptions in practically the same ratio. Moreover, both oxygen and

TABLE 7. *Occlusion of oxygen and argon at —183° and 76 cm. pressure in porous glass and Doucil containing nitric oxide.*

	Porous glass	" Doucil "
Vol. of NO sorbed	19·49	26·28
Vol. of O_2 sorbed	31·3	82·5
Vol. of O_2 sorbed in absence of NO	42·4	96·8
Vol. of A sorbed	25·9	53·1
Vol. of A sorbed in absence of NO	35·1	62·7
Decrease in O_2 sorption, %	26·2	13·9
Decrease in A sorption, %	26·2	15·3

* All volumes are in terms of cm.^{3} (at S.T.P.)/g.

argon sorptions were reversible, as is illustrated for porous glass in Fig. 5*d*. It can be concluded with both porous glass and Doucil that reaction between sorbed nitric oxide and oxygen is inappreciable at $-183°$. It has been shown (*loc. cit.*) that nitric oxide sorbed in either of these gels does not disproportionate at $-183°$, so that lack of reactivity is here associated either with loss of free-radical character of the nitric oxide on sorption or else the low temperature.

DISCUSSION

The gas-phase oxidation of nitric oxide has a negative temperature coefficient and has been studied down to —192° (Briner, Pfeiffer, and Malet, *loc. cit.*), so that the lack of reactivity of oxygen towards nitric oxide occluded in several sorbents is of considerable interest. Both Szego and Guacci (*Gazzetta*, 1931, **61**, 333) and Briner and Sguaitamatti (*Helv. Chim. Acta*, 1941, **24**, 421) found that oxidation of nitric oxide occurred in silica gel. Their results were obtained by using a streaming method in which nitrous gases diluted with air traversed the bed of silica gel. They are accordingly not fully comparable with those in the present paper in which nitric oxide was sorbed first and in which the sorbed nitric oxide exerted no gas pressure. The steps proposed by Briner and Sguaitamatti for oxidation are: adsorption of nitric oxide and oxygen; reaction to form nitrogen dioxide (catalysed by the gel); adsorption of nitrogen dioxide and dinitrogen trioxide. However, our demonstration that sorbed nitric oxide failed to react with subsequently sorbed oxygen may require a modification of this mechanism. Briner and Boubnoff (*J. Chim. phys.*, 1913, **11**, 597) also considered that the disproportionation involved the stage $4NO = 2N_2O + O_2$, and that nitrogen dioxide resulted by oxidation of adsorbed nitric oxide. This mechanism for the same reason may also need reconsideration.

According to the free energies of formation of the species involved (nitric oxide, nitrous oxide, and dinitrogen trioxide) disproportionation of nitric oxide should go virtually to completion. Reaction less than 100% must therefore represent a non-equilibrium state. Briner and Boubnoff (*loc. cit.*) and Briner, Biedermann, and Rotken (*ibid.*, 1926, **23**, 157) have demonstrated that disproportionation of nitric oxide is already excessively slow in the gas phase at room temperature. Compression or liquefaction of nitric oxide was considered to favour reaction, although we have been unable to detect any reaction in *solid* nitric oxide at —183° in 100 hr. However, nothing comparable with the rapid catalyses reported in this paper has hitherto been reported. There are also striking differences between the zeolites acting as disproportionation catalysts and the relatively feeble catalyses observed with siliceous gel sorbents. Evidently the intracrystalline environment of the zeolites, perhaps on account of the polar surroundings and comparatively intense fields of force within the crystals, is especially favourable in promoting reactivity. By contrast with nitric oxide, nitrous oxide remains unactivated by the intracrystalline field for sorption temperatures up to 350°. The very ready activation of nitric oxide is therefore likely to be connected with its free-radical character.

The sorption of nitrous oxide in chabazite was studied by Lamb and Ohl (*J. Amer. Chem. Soc.*, 1935, **57**, 2154), who determined a calorimetric sorption heat of 12,830 cal./mole, to be compared with the isosteric differential heats of Table 1. Seeliger's data (*Physikal. Z.*, 1921, **22**, 563) for sorption of nitric oxide in chabazite give evidence of irreversible phenomena, but no detailed comparisons with our results are possible.

Finally, it may be noted that at 0° and room temperature the chabazite–nitric oxide system was yellow, but at −183° it was violet. A similar colour sequence was found with the other zeolites and with Doucil and porous glass. A reddish hue at −78° and black at −183° has been reported for nitric oxide–silica gel, but these colours were regarded as having a physical origin and as being due to a fine dispersion of capillary condensate (Briner and Sguaitamatti, *loc. cit.*). However, the colours observed in chabazite cannot be of this kind since the interstitial channels in this mineral are not wide enough for capillary-condensed sorbate to appear. No colours were observed in our experiments with nitric oxide–silica gel.

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