89. *The Mechanism of Activated Diffusion through Silica Glass.*

By Richard M. Barrer.

Various observers have found that silica glass is permeable to gases, and that the diffusion rate increases exponentially with the temperature (*e.g.*, Williams and Fergusson, *J. Amer. Chem. Soc.*, 1922, **44**, 2160; van Voorhis, *Physical Rev.*, 1925, **23**, 557; T'Sai and Hogness, *J. Physical Chem.*, 1932, **37**, 2595). Alty (*Phil. Mag.*, 1933, **15**, 1035) applied the theoretical treatment of Lennard-Jones (*Trans. Faraday Soc.*, 1932, **28**, 333) to the problem, recognising the diffusion to be of the type recently found by a number of workers in this laboratory (Dunn, *Proc. Roy. Soc.*, 1926, **111**, 210; Wilkins and Rideal, *ibid.*, 1930, **128**, 394; Ward, *ibid.*, 1931, **133**, 513). In these communications it was shown that gases could diffuse along inter-crystalline boundaries or at higher temperatures through a crystal lattice. Diffusion obeyed Fick's law, and also the van 't Hoff isochore in that the diffusion process (velocity D) could be regarded as possessing a definite energy of activation E : $\partial \log D/\partial T = E/RT^2$.

Inter- and intra-crystalline diffusion possess different activation energies; *e.g.*, for oxygen–cuprous oxide the activation energies are respectively 9,200 and 15,200 cals./g.-mol. Lennard-Jones (*loc. cit.*) observed that different energies of activation would be anticipated for gases which are held to the surface by van der Waals forces, or by chemical forces, an electron switch having occurred in the latter case.

It is not clear in the gas–solid systems so far investigated which type of interaction has occurred, but in silica and silicate glasses there is every possibility of deciding between them, since the energetics of the migration of the rare gases may be used as standards of comparison, chemisorption being impossible. This investigation was designed to determine the mechanism of interaction and migration, and also to find the relative velocities and the activation energies for various common gases.

Apparatus.—The permeability of silica glass to various gases was followed by allowing gas to diffuse from an annular space into an internal silica vessel. The bulb used is shown diagrammatically in Fig. 1.

On all ground joints and taps Apiezon grease was employed. Ground joints near the furnace were water-cooled. The internal silica vessel and outer annular space were connected to mercury diffusion pumps and to a Hyvac pump. The furnace was made by winding nichrome about a central core and lagging with kieselguhr. Its length (about 1½ feet) enabled one to obtain a zone of constant temperature at its centre. By suitable series and series–parallel arrangements of resistances and regulating lamps, the total resistance of the furnace circuit was maintained constant, and any current required could be sent through it. The total current was maintained constant, and the furnace thermostatically controlled by iron-filament lamps. Any required temperature from about 100° to the fusion point of nichrome could thus be kept constant to within 1%. Temperatures were measured by means of a platinum–platinum-rhodium thermocouple, calibrated by observations of *E.M.F.* in metal-baths at their melting points. Pressure readings were taken by means of a McLeod gauge.

A good-quality silica glass was supplied by the British Thermal Syndicate. Hydrogen was generated electrolytically, and purified by passage over calcium chloride, palladium-coated copper at 340°, and phosphoric oxide. It was stored for use in large bulbs containing phosphoric oxide. For the diffusion experiments with air, the laboratory air was used without preliminary purification, the double-walled vessel was dispensed with, and a single-walled vessel employed. Nitrogen, argon, and oxygen were obtained from cylinders, and purified by passage through glass-wool, cotton-wool (to remove dust), soda-lime, and phosphoric oxide.

The silica vessel used for air possessed a diffusing surface of about 120 cm.^{2} and a thickness of 1·25 mm.; that used for hydrogen, nitrogen, and other gases had an area of *ca.* 80 cm.^{2} and a similar thickness of wall. In each case the gas diffused into a volume of 500 c.c. Since the external pressure was always about one atmosphere and the internal pressure small, the rate of leak at any one temperature was constant.

Results for a typical experiment with hydrogen were as follows: Temp., 713°; external press., 60·89 cm.;

Time (mins.)	38	65	114	131
Internal press. (cm. × 10^{-3})	6·8	12·0	19·7	24·6

Results.—In the following results, it will be observed that for some gases there is an increase in the energy of activation as the silica " ages "; and further experiments were conducted to find the reason for these effects.

FIG. 1.

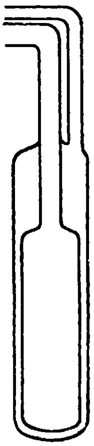
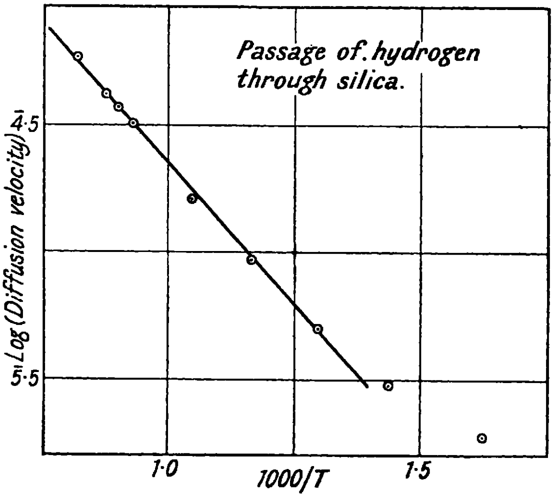


FIG. 2.



Hydrogen. Velocities of diffusion were measured at temperatures from 193° to 940°. The rate of diffusion is easily measurable at the lower temperature, although it is generally stated that permeability does not commence until nearly 300°. Diffusion of helium has been detected even at — 100° (see, *e.g.*, Burton, Braaten, and Wilhelm, *Canadian J. Res.*, 1933, **21**, 497).

The diffusion velocity was found by Wüstner (*Ann. Physik*, 1915, **46**, 1095) and by Williams and Fergusson (*loc. cit.*) to be proportional to pressure, as with helium (Burton, Braaten, and Wilhelm, *loc. cit.*). Several experiments with hydrogen at pressures of 61, 37, 26, and 12 cm. confirmed this result, which does not necessarily imply that hydrogen diffused as undissociated molecules. In the cases of air, oxygen, nitrogen, and argon, it was assumed that the same relationship held.

TABLE I.

[Rate = p(cm.)/t(mins.) here and throughout.]

Temp.	865°	833°	800°	676°	580°	496°	408°	378°	290°	193°	*579°	*713°	*940°
Rate × 10^4	4·12	3·65	3·17	1·58	0·92	0·50	0·30	0·185	0·062	0·013	0·87	2·34	5·75

* These determinations show the negligible effect of long heating upon the permeability of silica glass towards hydrogen.

Diffusion rates of hydrogen at 76 cm. pressure at a number of temperatures are summarised in Table I, the order being that in which they were determined, and the energy of activation was calculated from the graph in Fig. 2 to be as follows :

Temp. range	627—865°	579—940°
Energy (cals./g.-mol.)	10,900 (before prolonged heating)	10,800 (after prolonged heating)

Fig. 2 shows a deviation from the exponential form at low temperatures (Alty, *loc. cit.*).

Air. The measurements of diffusion of laboratory air are summarised in Table II. Assuming for the moment the validity of the theory of activated diffusion, and adopting the nomenclature of Alty (*loc. cit.*), one has for each gas in a mixture

$$\mu = Bpe^{-(W_0 + E_0)/RT}$$

(μ = permeability; B = a constant; $W_0 + E_0$ = activation energy for diffusion = term due to overlapping fields + term proportional to heat of adsorption). For air, a binary mixture, one measures

$$\mu = \mu_{O_2} + \mu_{N_2} = B_{O_2}p_{O_2}e^{-(W_{0O_2} + E_{0O_2})/RT} + B_{N_2}p_{N_2}e^{-(W_{0N_2} + E_{0N_2})/RT}$$

which will not generally give a straight line when log μ is plotted against the reciprocal of the absolute temperature; in fact, the relevant curve is not linear even at high temperatures, but this result is due, not to the above mixture law, but to the effects of prolonged heating, as may be seen by comparing measurements 12, 11, and 10 with 3, 1, and 6, respectively, and from Fig. 3: the flowing curve is drawn as far as possible through points obtained in consecutive measurements.

FIG. 3.

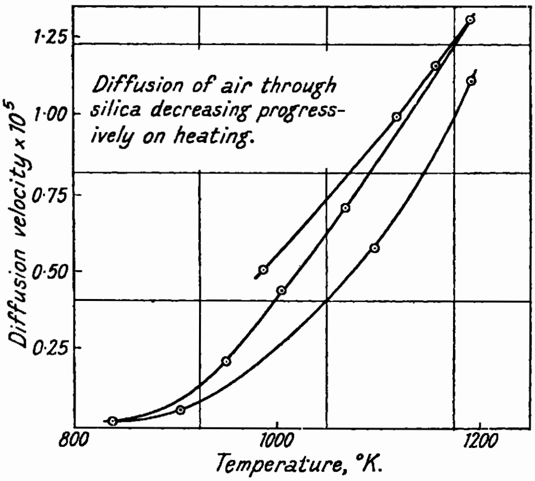


TABLE II.

Order	1	2	3	4	5	6	7	8	9	10	11	12
Temp.	715°	846°	884°	917°	678°	422°	796°	732°	632°	566°	826°	920°
Rate × 10^5 ...	0·51	1·00	1·18	1·30	0·184	0·028	0·712	0·44	0·056	0·010	0·60	1·12

With decreasing velocity there is evidence of increased activation energy.

From the data, the following apparent activation energies are calculated; they should lie between those for nitrogen and oxygen.

Measurement nos.	4 and 5	11 and 12
Energy (cals./g.-mol.)	18,500	22,000

Helium. Our results in the range from room temperature to 936° are given below in the order in which they were made. The external pressure was 76 cm. All the points fall on

Temp.	849°	756°	613°	516°	281°	17°	262°	473°	668°	883°	936°
Rate × 10^4	4·54	3·82	2·36	1·55	0·318	0·0035	0·308	1·10	2·66	4·60	5·20

the straight line of Fig. 4 or on this line produced. It appears that, as for hydrogen, the value of the activation energy is a fundamental constant for the diffusion process through silica glass, a value which is altered only by increasing silicate content in a glass and not by prolonged heating, as shown by the last five measurements (see also Table III). The graph in Fig. 4

gives the activation energy for diffusion as 5,780, in agreement with the calculations of Alty from the data of T'Sai and Hogness (5,560 cals./g.-mol.). There is no decrease of the energy at the lowest temperatures (17° and 262°) as noted with hydrogen on a *fresh* silica surface.

Nitrogen. A series of measurements was made with cylinder nitrogen, and the same silica vessel which had been used for the run with hydrogen. Although the latter gas had shown no decrease in permeability in this vessel, yet for nitrogen, the rates, initially comparable with those for air, decreased even more rapidly than those for air with time of heating. The external pressure was 76 cm.

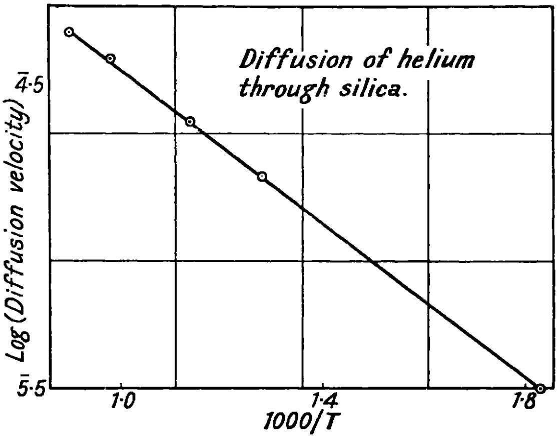
Measurement no. ...	1	2	3	4	5	6	7	8
Temp.	940°	850°	*752°	*752°	648°	*945°	850°	*940°
Rate × 10^5	1·00	0·47	0·203	0·119	0·041	0·48	0·135	0·26

* Figures showing decrease in permeability as heating proceeded.

Owing to the falling rate, the activation energies can be calculated only from consecutive measurements; nos. 1 and 2 give 22,100 cals./g.-mol., and the mean of nos. 6, 7 and 7, 8 is 29,900 cals./g.-mol. As for air, there seemed to be a definite increase in the energy of activation as the period of heating of the silica glass was prolonged.

Although it is not possible to represent the foregoing results in the usual graphical form, the data of Johnson and Burt (*J. Opt. Soc. Amer.*, 1922, **6**, 734), who apparently did not encounter decreasing permeabilities, show that the exponential temperature coefficient obtains with precision between 600° and 900°. The energy of activation computed from their data is 26,000 cals./g.-mol. in substantial agreement with our own calculations.

FIG. 4.



Oxygen. This gas diffused through fused silica at a speed comparable with that for nitrogen. The results for an external pressure of 76 cm. are shown below.

Temp.	944°	870°	938°	848°	680°	771°
Rate × 10^5	0·61	0·186	0·367	0·114	0·05	0·087

From measurements 2 and 3 and 3 and 4 in pairs, the activation energy is calculated as 27,600 and 35,200 cals./g.-mol. respectively (mean, 31,4000 cals. between 840° and 940°). It was impracticable to plot a curve.

Argon. Measurements with this gas are summarised below in the actual order of determination (external pressure 76 cm.). From series A and B the calculated energy is 48,000 and 32,100 cals./g.-mol. respectively. Series A was measured with a silica glass which, owing to very prolonged heat treatment, had almost entirely lost all porous properties towards such gases as oxygen, argon, and nitrogen. Series B was measured with exactly the same glass which had had a brief treatment with hydrofluoric acid as described below.

	Series A.	
Temp.	940°	1000°
Rate × 10^8	1·15	3·83

	Series B.		
Temp.	943°	860°	943°
Rate × 10^5	0·424	0·119	0·200

DISCUSSION.

Mechanism of Diffusion.—It has been shown that for all the gases save hydrogen and helium permeability decreases strongly with time of heating. It was found, however, that treatment of the silica glass with hydrofluoric acid restored the original porosity; hence, the decrease in diffusion rate and the accompanying increase in energy of activation (Table III) were caused by a surface layer. This fresh surface phase was not due to formation of silicates from metalliferous dust, since its occurrence was independent of the

TABLE III.

Activation Energies.

Gas.	Nature of glass.	Authors.	Energy, cals./ g.-mol.	Remarks.
He	Fused silica	T'Sai and Hogness	5,600	The activation energy increases as the amount of silicate increases.
	,, ,,	Barrer	5,700	
	Pyrex	van Voorhis	8,700	
	Thuringian	Piutte and Boggiolera	11,300	
Ne	Fused silica	T'Sai and Hogness	9,500	
H_2	Fused silica, Tube I	Williams and Fergusson	9,300	
	,, ,, ,, II	,, ,, ,,	10,000	
	,, ,, ,, III	,, ,, ,,	10,000	
	,, ,, ,, IV	,, ,, ,,	10,800	
	,, ,, ,, I	Barrer	10,900	
	,, ,, ,, I (superficially crystallised)	,,	10,800	Second value after prolonged heating.
	Fused silica	Mayer	8,500	
	,, ,,	Johnson and Burt	9,200	
	,, ,,	Wüstner	12,000	At *ca.* 800 atm.
	Pyrex	Williams and Fergusson	*	Activation energy and permeability profoundly altered by the presence of silicates.
	Jena	,, ,, ,,	†	
N_2	Fused silica	Johnson and Burt	26,000	
	,, ,,	Barrer	22,000	
	,, ,, (superficially crystallised)	,,	29,900	
O_2	Fused silica	Barrer	31,200	A superficially crystallised silica was cleaned with HF and reheated.
Air	Fused silica	Barrer	18,500	An apparent activation energy only. A different silica glass from that used in other measurements.
	,, ,, (superficial crystallisation commencing)	,,	22,000	
A	Fused silica (superficially crystallised)	Barrer	48,000	Difficult to determine with accuracy owing to slow rate of diffusion.
	Fused silica	,,	32,100	Fresh surface obtained with HF.

* Activation energy not obtainable. † Permeability negligible.

purity of the gases; further, no decrease was observed for hydrogen and helium, whose velocity of diffusion is, of course, decreased by silicate formation (Table III).

It was therefore concluded that the new surface phase was crystalline (in fact, such a structure was observed as a cloudiness of the surface layer). Crystallisation in this way was accompanied by a decrease in width of intercrystalline slip-planes, probably occasioned by surface fusion of tiny crystallites. The gases hydrogen, helium, and neon, with small energies of activation for the migration, passed easily through the crystal lattice of crystalline silica or the less symmetrically arranged micelles of " amorphous " silica glass. Oxygen, nitrogen, argon, and air, however, whose main passage was down slip-planes, were very sensitive to alterations in the width of such planes. The diffusion in these cases may be likened to the uptake of hydrogen by copper (Ward, *loc. cit.*). It is important to note in Table III (i) that the activation energy for hydrogen in a whole series of silica glasses is remarkably constant, and (ii) that there is close agreement for the energy for helium between our experiments and those of T'Sai and Hogness. The values of these energies for hydrogen, helium, and neon should, according to this theory, be fundamental constants for the diffusion process through each form of silica and would vary according to the crystal habit considered. Fused silica glass (Zachariasen, *J. Amer. Chem. Soc.*, 1932, **54**, 3841) is the most open of all silica structures. Tetrahedral symmetry of the silica and oxygen atoms is still preserved; spatial periodicity, however, is lacking, and the silica-oxygen chains cross one another irregularly, thus forming rings containing both less and more than 12 atoms. β-Cristobalite (see " Strukturberichte," 1931, pp. 166—172) is the most open crystal structure of silica; the high-temperature form appeared as a very thin cloudy layer on the fused silica surface when this was heated (cf. Williams and Fergusson, *loc. cit.*). In cristobalite, systems of zig-zag chains cross one another and form wide 12-membered rings, of diameter 6 Å. β-Tridymite resembles β-cristobalite in ring formation and ring diameter. Quartz, however, consists of spiral chains branching in all directions; no rings are formed, the packing density is much greater, and the widest "hole" in the lattice appears to be about 4 Å. Activation energy is accordingly much greater for lattice migration in quartz than for the other structures. Urry (*J. Amer. Chem. Soc.*, 1933, **55**, 3242) found no trace of helium migrating through a single quartz crystal at room temperature.

Those gases which at high temperatures show lattice migration (the term "lattice" including the irregular framework of fused silica) should at low temperatures show slip-plane migration, since in this region the migration depending more upon the temperature will become negligible. The decrease in the energy of activation which has been observed for hydrogen is ascribed to this cause. Alty (*loc. cit.*) has ascribed it to the character of the diffusion equation (after Lennard-Jones) :

$$\mu = A n_0 \bar{C}^2 \tau_0 e^{-E_0/KT} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

where τ_0 is the period of vibration of an adsorbed atom perpendicular to the surface; $E_0 = \frac{1}{2}mC_0^2$ is the energy to be given to an adsorbed atom to render it mobile on an external surface; and

$$\bar{C} = C_0 + \left(\frac{\pi KT}{2m}\right)^{\frac{1}{2}} e^{-mC_0^2/2KT}$$

is the average velocity of the mobile atoms along the surface.

Equation (1) will reduce to the simple exponential form $\mu \propto n_0 e^{-E_0/KT}$ only where $KT \ll E_0$; if $KT \gg E_0$, we have $\mu \propto n_0 T e^{-E_0/KT}$.

In this system we can make a critical experiment, which decides against this explanation. The falling energy with decrease in temperature is given also by helium (T'Sai and Hogness) : a silica tube was accordingly given a prolonged heating, but measurements with helium then showed no decrease in the energy as the temperature was lowered to room temperature. The calculation between 17° and 262° gave a value 5,670 cals./g.-mol. as compared with 5,780 at high temperatures. Therefore, by destroying slip-planes we have destroyed the effect, which must accordingly be ascribed to slip-plane diffusion only.

For glasses showing slip-plane diffusion at low temperatures the calculations in Table IV have been made by using the integrated van 't Hoff isochore $\log_e \mu_1/\mu_2 = E/R \, . \, (1/T_1 - 1/T_2)$ over the temperature range specified; our result for helium shows that this is applicable at least to 0°.

TABLE IV.

Gas.	Glass.	Worker.	Nature of diffusion.	Energy.	Temp.
H_2	Fused silica	Barrer	Lattice	10,800	>400°
		,,	Slip-plane	4,300	193
He	Fused silica	T'Sai and Hogness	Lattice	5,700	>300
		Burton, Braaten, and Wilhelm	Slip-plane	4,190	110—0
				3,040	0 to −41
				2,310	−41 to −78
He	Pyrex	van Voorhis	Lattice	8,100	>300
		Urry	Slip-plane	5,840	282—172
				4,540	172—81

Generally, diffusion rates are proportional to total gas pressures. The results of Urry (*J. Amer. Chem. Soc.*, 1932, **54**, 3887) are, therefore, valuable as showing a pressure dependence, $\mu = \alpha P^n$, at constant temperature for Pyrex, lead glass, soda glass, and Jena 16''', for they indicate that diffusion rates are governed by surface concentrations, not by *direct* entry into the glasses by molecules from the gas phase (cf. Alty, *loc. cit.*). The effect of the introduction of large alkali ions as in the formation of silicate glasses is to reduce the space available for lattice migration, and so to increase the energy of activation. The phenomenon is similar to that observed by Rabinowitsch (*Nature*, 1933, 640), who showed that the persorption of dehydrated chabazite by nitrogen and hydrogen could be much modified by ionic exchange of calcium for sodium or potassium. The large alkali ions can render pores already of molecular dimensions too small for penetration.

The manner in which energies for slip-plane migration decrease with temperature suggests a range of sizes of slip-planes, and provides a satisfactory picture of the selective activated flow of the gas into slip-planes of decreasing sizes with rise of temperature. This process of activated up-take has been proposed (*e.g.*, Ward, Faraday Society Discussion, 1932) to explain the rising part of isobars such as those for hydrogen and nickel. The present work supports this view for those systems wherein the sorption is not of chemical nature.

Nature of Solid–Gas Interaction during Migration.—It has to be decided whether any of the gases investigated migrate from chemisorbed states, are dissociated, or are held only by van der Waals interaction. To explain the experimental results of slip-plane and lattice diffusion at least two factors must be considered. The first may be referred to as the space factor, dependent upon the relative magnitudes of migrating atom and lattice or intercrystalline dimensions; the second will depend on the heat of adsorption—the adsorption factor. A mathematical analysis which considers the activation energy as composite should then satisfy the experimental data.

Helium, neon, and hydrogen have a relatively small space factor contribution, and for helium and neon only physical adsorption can occur. Any change in the nature of the adsorption process from van der Waals to chemisorption should be reflected in an increased activation energy. Accordingly, for hydrogen the interaction appears to be physical. The heavier gases have relatively large energies for migration. However, argon (32,100—48,000) has the greatest energy of all, and physical processes only are possible. The energies of interaction in these cases are, therefore, most readily interpreted on a purely physical basis by the increase in the space factor, dependent upon repulsive forces of closest approach. The equations of state for the different gases investigated in the diffusion experiments lead to the following type of interaction law on mutual approach of two atoms of the gas (Lennard-Jones, *Proc. Physical Soc.*, 1931, **43**, 474) :

$$E = \lambda_{\text{rep.}} R^{-(n-1)}/(n-1) - \lambda_{\text{att.}} R^{-6}/6$$

where E denotes the potential energy, $\lambda_{\text{rep.}}$ the repulsive force constant, $\lambda_{\text{att.}}$ the attractive force constant, R the distance apart, and n is an integer to be determined by experiment.

For $n = 13$, Lennard-Jones (*loc. cit.*) has given the following data on the permanent gases :

Gas.	$\lambda_{\text{rep.}}$.	$\lambda_{\text{att.}}$.	Calculated heat of sublimation at 0° K., cals./g.-mol.	Observed heat of sublimation.
He	$4{\cdot}55 \times 10^{-105}$	$7{\cdot}43 \times 10^{-60}$	126	—
Ne	$4{\cdot}36 \times 10^{-104}$	$5{\cdot}07 \times 10^{-59}$	612	590
H_2	$7{\cdot}79 \times 10^{-104}$	$6{\cdot}3 \times 10^{-58}$	529	—
N_2	$4{\cdot}44 \times 10^{-102}$	$8{\cdot}38 \times 10^{-58}$	1640	1860
A	$2{\cdot}13 \times 10^{-102}$	$6{\cdot}50 \times 10^{-58}$	2030	2030

It is obvious that the energy for gas–silica interaction follows very closely, not only in the order, but also in the ratio of the magnitudes of the corresponding gas–gas interaction; for instance, in each case one may bracket hydrogen and neon as behaving similarly, and nitrogen and argon. The evidence of these force fields, calculated and observed, suggests very strongly that the phenomenon is one of dynamic polarisation, coupled with exchange forces which cause a powerful repulsion (the space factor contribution) and follow in the order of interactions of the van der Waals type. A further argument against migration of the gases as atoms is that the heat of dissociation of nitrogen is much greater than that of oxygen, yet their activation energies and migration rates are similar.

The above interaction law furnishes interesting information on the magnitude of the energies and the pore diameters to be expected. It has been applied to calculate energies of activation for migration of a gas atom of helium, hydrogen, and argon through four similar atoms arranged in a square of a given diameter.* The magnitudes of the energies

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* These calculations have been made at the suggestion of Professor Lennard-Jones, to whom the author is very grateful.

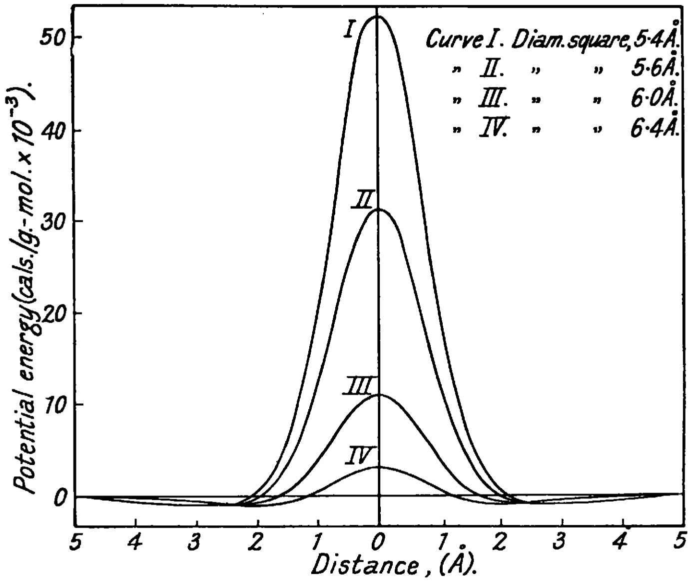
required to bring the gas atom from infinity to the plane of the square are given in Table V, and the graphs in Fig. 5 show a few of the potential-energy curves for the migrating atom as it approaches the plane of the square.

TABLE V.

Diameter of square, Å.	Energies (cals./g.-mol.).			Diameter of square, Å.	Energies (cals./g.-mol.).		
	He.	H_2.	A.		He.	H_2.	A.
3·6	13,920	—	—	6·0	−57·1	—	10,750
3·8	8,393	—	—	6·2	—	−203·4	5,975
4·0	4,250	—	—	6·4	−47·8	—	3,089
4·2	2,183	44,060	—	6·6	—	−246·1	1,296
4·4	1,078	23,910	—	6·8	—	—	187
4·6	—	13,070	—	7·0	−32·5	—	−315
4·8	217	7,123	—	7·2	—	−200	−713
5·0	75·0	3,825	147,100	7·4	—	—	−885
5·2	−2·1	1,936	87,120	7·6	—	—	−950
5·4	−39·1	916	52,290	7·8	−21·4	−130	−954
5·6	−54·3	352	31,230	8·6	−10·8	—	−735
5·8	—	40	18,520	10·8	—	—	−237

FIG. 5.

Potential-energy curves for migration of an argon atom through a square of argon atoms.



From the calculations we deduce that (1) for reasonable pore sizes, the energies are of the magnitudes met with in experiment; (2) for helium and hydrogen, lattice migration should occur readily, as shown experimentally; (3) the diameters of the slip-planes which condition the migration of argon are of the same order of magnitude as the largest dimensions of the lattice (6 Å.); (4) when the critical diameter is approached, the activation energies become exceedingly sensitive to small alterations in pore diameter, *e.g.*, for helium, 0·2 Å. (from 4·0 to 4·2 Å.) causes a change in energy from 4,200 to 2,000 cals./g.-mol., values to be compared with the high- and low-temperature energies of migration of helium through silica; (5) if a 12-membered ring (as occurs in the silica structure) of the same diameter as a square were substituted for the square, the energy of activation would be trebled: according to (4) this would not cause a material alteration in pore size.

These models are only approximate ones since the law of interaction between gas and silica is not known, but they serve to demonstrate the nature and properties of the diffusion very clearly.

The conception of the process of migration developed here differs in one important respect from the earlier theory of Alty. We incline to the view that the atom or molecule is to be considered as migrating in one act over a *single* potential barrier which could be regarded mathematically as composed of two energies. This barrier recurs throughout the periodic structure of the solid. Previously, the energy was regarded as made up by two *separated* barriers, of which one, that due to overlapping fields (the space factor), did not contribute to flow at any point save the entrance to a pore. The diffusion equation can now be written in the form

$$\mu = AN_0\bar{C}^2\tau_0 e^{-E_T/KT}$$

where $E_T = (E_0 + W_0) =$ total energy of activation, W_0 being the energy required to overcome the repulsive forces due to exchange forces in the solid, *i.e.*, the space factor contribution, and the other terms being as previously stated. There will clearly be no deviation from exponential form, for in all cases $E_T \gg KT$, and hence $\bar{C} = C_0$, or $\mu \propto e^{-E_T/KT}$ at all temperatures in accordance with experiment.

SUMMARY.

(1) Measurements have been made of the velocity of diffusion of helium, hydrogen, oxygen, nitrogen, argon, and air through fused silica glass at temperatures ranging between room temperature and 1000°.

(2) For all these gases the same type of exponential temperature coefficient has been observed as has previously been found for helium and neon. Energies of activation for diffusion have been calculated ranging from 5,780 cals./g.-mol. for helium to 32,000 cals. and higher for argon. These energies have been compared with energies calculated from the data of other workers.

(3) The diffusing gases can migrate according to two mechanisms. Helium, hydrogen, and neon can pass through the " lattice " of fused silica at high temperatures. The heavy gases oxygen, nitrogen, and argon migrate mainly through slip-planes. At low temperatures helium, hydrogen, and neon also show slip-plane diffusion. There is evidence that migration proceeds from the adsorbed layer, not directly from the gas phase.

(4) The interaction has been shown to be physical, and the gases migrate as undissociated molecules. The activation energies are due to dynamic polarisation resulting in van der Waals cohesion, and to exchange forces resulting in gas–solid repulsions.

(5) Calculations have been made employing the known laws of interaction of hydrogen, helium, and argon which give energies of the correct order for reasonable pore diameters, and indicate " lattice " migration for helium and hydrogen.

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