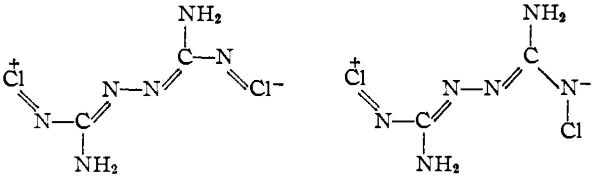
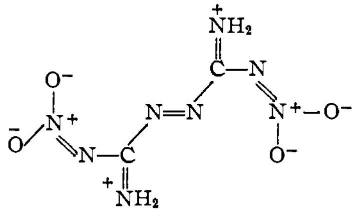
ing forms involving conjugation clear across the molecule are possible.

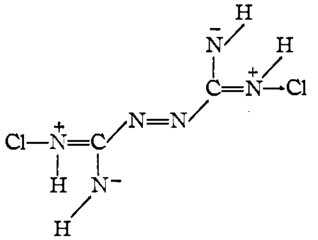


Such a situation is not present with the nitro compound for here only local conjugation is possible and the central double bond is still present in the form with a separation of charge.



Thus the chlorine compound should have a low lying excited state of more stability than the nitro compound and consequently absorb at longer wave length and with greater extinction.

With structure (2), it is not possible to write forms with a separation of charge involving oscillations clear across the molecule



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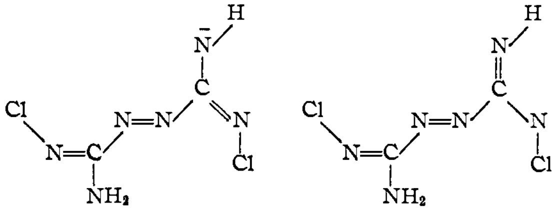
and so this structure does not account for the observed ultraviolet spectra. Structure (3) simply changes the position of the double bonds at the ends of the conjugated system in (2) so that there would be no long oscillations in going from (2) to (3) and hence the absorption would be at relatively short wave lengths.

The spectra then suggest the compounds have structure (1) with the chlorine and nitro groups attached to doubly bonded nitrogen atoms.

Another way of considering this problem is to suppose a proton dissociates from either structure (1) or structure (2). The resulting ion in either case is the same resonance hybrid.



When a proton returns to this ion two different molecules can be formed depending on to which nitrogen it returns. It will go to the nitrogen of greatest basicity which is expected to be the one to which the hydrogen is attached rather than the one to which the much more electronegative chlorine atom is attached. On the basis of this reasoning, the structure of the compound should be (1) and not (2). The same reasoning also favors the similar nitrimine structure for the nitro compound. This method of approach is thus in agreement with the deductions from the ultraviolet spectra that the compounds are chloroimines and nitrimines. The dipole moment data suggest the azo linkage is *trans.*

SAN FRANCISCO, CAL.

[CONTRIBUTION FROM LOS ALAMOS SCIENTIFIC LABORATORY, UNIVERSITY OF CALIFORNIA]

Permeability and Solubility of He^3 and He^4 in Vitreous Silica[1]

BY W. M. JONES

RECEIVED MARCH 5, 1953

The relative permeabilities and solubilities of He^3 and He^4 in vitreous silica have been measured as a function of temperature, and the differences in the diffusion activation energies and heats of solution evaluated. The absolute permeabilities and solubilities also were obtained.

I. Relative Permeabilities and Solubilities

Introduction.—It was considered of interest to measure the relative permeabilities and solubilities of He^3 and He^4 in vitreous silica at several temperatures, particularly with regard to a possible small difference in diffusion activation energies and its relationship to the theory of rate processes.

Apparatus and Materials.—The main features of the permeability apparatus used at the five highest temperatures are given in Fig. 1. The He^3–He^4 mixture was contained inside the hollow sphere A communicating with an input measuring and transfer system through the 0.7-mm. bore capillary D. Gas diffused from the sphere into the space C, from which it was frequently transferred through F to a second measuring system. The seal E at room temperature was made with Armstrong cement. Copper-wool between A and B was found by differential thermocouple measurements to bring A to the temperature of the surrounding bath. The stirred bath of silicone fluid or of fused lithium, sodium and potassium nitrates in eutectic proportions was regulated to ±0.05° or better. Temperatures were measured with a NBS calibrated platinum resistance thermometer which was protected from the bath with a thin, close-fitting platinum sheath. At 0° a crushed ice-bath was used. The apparatus used at 356.8 and 273.16°K. was similar to that in Fig. 1, except that the collection jacket was Pyrex and its connection to the capillary D was made a short distance above the sphere with a graded seal. The spheres were prepared from clear fused quartz. Volume, weight, density and micrometer measurements were made. The spheres were about 3.8 cm. o.d. The average wall thickness of the sphere at the lowest two temperatures

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(1) This work was sponsored by the A.E.C.

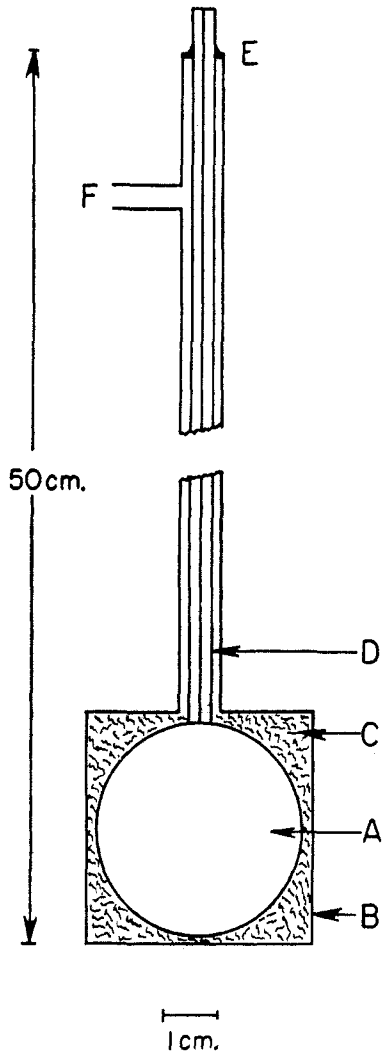

Fig. 1.—High temperature diffusion apparatus: A, hollow quartz sphere; B, steel jacket; C, collection space filled with copper wool; D, capillary lead from filling system to sphere; E, glass to metal seal (Armstrong cement); F, lead to collection measurement system.

was slightly over 0.01 cm., and the He^3 to He^4 ratio of the starting material was about 1:1. For the sphere used at the highest five temperatures, the corresponding values were slightly under 0.2 cm. and approximately 1:4. Analyses were made with a Consolidated-Nier mass spectrometer with an improved output meter to allow more precise peak height measurement. Magnetic scanning was used.

In the solubility measurements, about 50 cc. of vitreous quartz was allowed to come to equilibrium with an approximately 1:1 mixture of He^3–He^4 at a total pressure of about one atmosphere in a steel can of about 100-cc. volume provided with a hypodermic needle filling tube. For the highest temperature, the quartz was in the form of discs of 3.5 mm. thickness. At the remaining two temperatures, particles were used which passed a No. 30 sieve but not a No. 40 sieve.

Procedure and Results.—With the outgassed and evacuated diffusion assembly at bath temperature, a quantity of He^3–He^4 gas, estimated to give a pressure of about 60 cm. in the sphere, was withdrawn from a storage bulb and transferred to the sphere with a Toepler pump. There should have been no isotopic separation effects due to the manner of taking the sample, flow through the capillary to the sphere, or thermal diffusion. The diffused gas was frequently transferred by a Toepler pump from the jacket to a small constant volume manometer for measurement until about 0.25 cm.^{3} gas had been collected. Two such samples were taken at 798.3°K. and three at the other temperatures. The amount of gas in the storage bulb before and after transfer gave the initial amount of gas in the sphere, and the final content of the sphere also was measured. The diffused samples and portions of the initial and final sphere gas pertaining to a given temperature were analyzed for impurities and isotopic composition in a single sitting at the spectrometer under as nearly identical conditions as possible.

The ratio of sample to total gas and the ratio of isotopic permeabilities are such that the latter is given with satisfactory accuracy by

$$P_3/P_4 = (He^3/He^4)_{sample}/(He^3/He^4)_{av} \qquad (1)$$

in which $(He^3/He^4)_{av}$ is the isotopic ratio of the sphere gas at the mid-point of the sampling period, found by linear interpolation between the initial and final values. The uncertainty in P_3/P_4 should be limited by the precision rather than absolute accuracy of the spectrometer. Individual peak heights were determined to about 0.25%, or better, and the spectrum was scanned repeatedly. Column 2 of Table I gives P_3/P_4 with mean deviation uncertainties. A plot is given in Fig. 2.

TABLE I

PERMEABILITIES OF He^3 AND He^4

T, °K.	(P_3/P_4), obs.	$P_4 \times 10^9$, obs.
798.3	1.124 ± 0.005	1.66
682.3	1.125 ± .003	0.900
568.4	1.114 ± .004	.421
472.6	1.100 ± .005	.166
425.6	1.096 ± .006	.0897
356.8	1.078 ± .003	.0294
273.16	1.053 ± .002	.00332

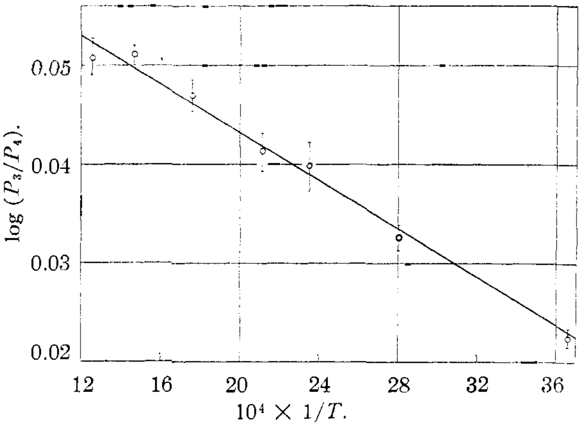

Fig. 2.—Relative permeabilities of He^3 and He^4.

In the solubility measurements, the times allowed for equilibrium were such as to give at least 99.9% saturation at the most interior points of the largest pieces of silica. The steel can was then rapidly immersed in liquid nitrogen and the undissolved helium removed with a Toepler pump. The dissolved gas, amounting to about 0.5 cc., was then released by bringing the solubility can to about 350°. An experimentally determined correction was made for adsorption of the He^3–He^4 mixture with the silica sample and container at liquid nitrogen temperature. This correction amounted to about 2% for the finely divided silica and was much less for the other sample. Analysis of the adsorbed gas showed that the correction for isotope effects could be neglected. The gas measurements and spectrometer analyses were made as in the permeability measurements. The relative solubility of He^3 with respect to He^4 is $S_3/S_4 = (3/4)_{quartz}/(3/4)_{gas}$ and is given in Table II along with the absolute solubility of He^4 expressed as cc. He^4 N.T.P. per cc. silica at one standard atmosphere pressure, assuming Henry's law and a quartz density of 2.207 g./cm.^{3} (from measurements by Archimedes' method on the diffusion spheres and the material from which they were made). The absolute solubilities should be correct to about 0.5–1%. The S_3/S_4 probable errors in Table II are based on statistical analysis of all the solubility mass spectral data. The improved precision over the P_3/P_4 data is due partly to the fact that a single value could be used for $(^3/_4)_{gas}$, based on analysis of four different samples.

TABLE II

SOLUBILITIES OF He^3 AND He^4

T, °K.	S_3/S_4	S_4, cc. N.T.P. (cc. silica)$^{-1}$ atm.$^{-1}$
672.8	0.998 ± 0.003	0.00859
422.0	.994 ± .002	.01262
313.5	.993 ± .002	.01848

Discussion

Using least squares, the data of Tables I and II may be represented by $P_3/P_4 = (1.170 \pm 0.004)\ e^{-(57 \pm 2)/RT}$ and $S_3/S_4 = (1.003 \pm 0.003)\ e^{-(6 \pm 2)/RT}$. Since $D = P/S$ (see below), $D_3/D_4 = (1.167 \pm 0.005)\ e^{-(51 \pm 3)/RT}$. Uncertainties are precision probable errors.

The data suggest a slightly larger heat of solution for He^4, in accord with its lower vibrational energy in the potential wells in which dissolved atoms are localized. However, the effect is barely outside of experimental uncertainty. The diffusion process may be considered in terms of the passage of a He atom from one potential well to another through an intermediate state. From an idealized treatment of diffusion,[2] it may be shown that the ratio of diffusion coefficients D_3/D_4 should be given approximately by

$$D_3/D_4 = (\nu_3/\nu_4)e^{-(\Delta G_3 - \Delta G_4)/RT} \qquad (2)$$

Here ν_3 and ν_4 are the vibrational frequencies of the isotopes in the potential wells, while ΔG_3 and ΔG_4 are the molal Gibbs free energy increments when the solute is brought from a potential well to an intermediate state under the restriction that solute atoms move in a plane normal to the reaction or diffusion path over the potential energy barrier (for details, a discussion in terms of more conventional absolute rate theory, and a comparison of the treatments, see ref. 2). From equation (2) we may find the corresponding difference in heats of activation, $\Delta H_3 - \Delta H_4 = -R\,\mathrm{d}\ln(D_3/D_4)/\mathrm{d}(1/T)$, which amounts to plus 51 cal. This quantity should be approximately the vibrational energy excess of He^3 over He^4 in the intermediate state minus the corresponding excess in the well. Neglect of vibrational energy in the intermediate state would lead one to the incorrect prediction that He^4 would have the larger heat of activation. In the approximation that the light solute atoms may be regarded as vibrating harmonically against a massive lattice, the ratio ν_3/ν_4 should be 1.155, the square root of the inverse mass ratio. The difference between this value and the experimental value, even if real, does not admit of a unique explanation, since equation (2) is only an approximation for a model which itself cannot strictly apply to fused quartz.

II. Permeability and Solubility of He^4

For steady state flow through a spherical shell of internal and external radii r_1 and r_2, a permeability P may be defined by

$$P = F(r_2 - r_1)/4\pi r_1 r_2 p \qquad (3)$$

where F is the observed flow rate when the gas pressure is p and the diffusion is into a vacuum. Account was taken of decreasing pressure in the sphere, impurities in sphere and sample gases, and diffusion through the capillary, recognizing the temperature gradient. The geometric mean of the internal and external areas was used in place of $4\pi r_1 r_2$ in correcting for the fact that the diffusion media were slightly oblate ellipsoids of revolution. Values of P_4 in Table I and Fig. 2 were obtained using values for the mixture, P_3/P_4, and the sphere gas composition. Permeabilities are in units of cm.^{3} N.T.P. per second per cm.^{2} per mm. for a one-mm. wall. For the spheres used, the accuracy in P_4 is estimated at 2%, excluding error introduced by any difference between the average of the reciprocal wall thickness and the reciprocal of the average thickness which was used. The spheres appeared to be of rather uniform wall thickness, but they were not broken for examination. A rectangular distribution of wall thickness with a 10% half width would cause the average of the reciprocal thickness to exceed the reciprocal of the average by less than 1%.

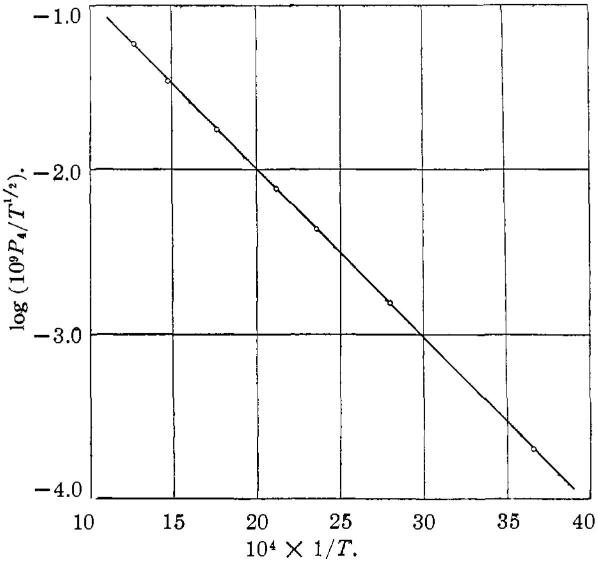

Fig. 3.—Permeability of He^4.

There is a mean deviation of about 15% among the present permeabilities, those of Tsai and Hogness,[3] and those of Braaten and Clark.[4] Barrer's[5] values are lower by almost a factor of ten. The permeabilities were fitted by $10^9\ P_4 = 1.143\ T^{1/2}\ e^{-4700/RT}$. Values of $-R\,\mathrm{d}\ln(P_4/T^{1/2})/\mathrm{d}(1/T)$ are given in Table III. There is some arbitrariness in the data fitting, so that the good agreement is illusory.

TABLE III

Observer	Temp. range, °C.	$-R\mathrm{d}\ln(P_4/T^{1/2})/\mathrm{d}(1/T)$, cal. mole^{-1}
Tsai and Hogness	180–955	4700
Braaten and Clark	80–562	4730
Barrer	17–936	4800
Present data	0–525	4700 ± 75

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[2] (a) C. A. Wert, *Phys. Rev.*, **79**, 601 (1950); (b) C. Zener in "Imperfections in Nearly Perfect Crystals," John Wiley and Sons, Inc., New York, N. Y., 1950.

[3] L. S. Tsai and T. Hogness, *J. Phys. Chem.*, **36**, 2595 (1932).

[4] F. O. Braaten and G. Clark, THIS JOURNAL, **57**, 2714 (1935).

[5] R. M. Barrer, *J. Chem. Soc.*, 378 (1934).

The solubility of He^4 in Table II is represented by $S_4 = 4.438 \times 10^{-3}\ e^{885/RT}$. Williams and Ferguson[6] obtained solubilities of 0.0101 and 0.0103 at 515 and 445°. The diffusion coefficient D is given by the right-hand side of equation (3), provided p is replaced by c, the concentration of He in silica at the inner surface of the sphere. Since $c = sp$, where s is the solubility, we have $D_4 = P_4/S_4 = 2.575 \times 10^{-7}\ T^{1/2}\ e^{-5585/RT}$ cm.^{2} sec.$^{-1}$.

A plot of log P or log D against $1/T$ is slightly concave up, as has previously been observed in this and other cases.[3–5] Such behavior might be due to a small admixture of slip-plane diffusion of lower activation energy than the main process of lattice diffusion.[5] The curvature mentioned might be partly connected with a theoretical inadequacy in the choice of the pre-exponential term even if there were a well-defined activation energy. Such an effect would be emphasized by the relatively small activation energy. The curvature may also be due to the fact that the distributed nature of the parameters defining a glass gives rise to a corresponding spectrum of activation energies. The tendency of lattice expansion to give a lower activation energy at high temperatures is probably small with quartz.

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[6] G. A. Williams and J. B. Ferguson, THIS JOURNAL, **46**, 635 (1924).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

A Convenient Source of Gamma Radiation

BY DONALD F. SAUNDERS, FREDERICK F. MOREHEAD, JR., AND FARRINGTON DANIELS

RECEIVED OCTOBER 15, 1952

A simple irradiator is described which gives intense and uniform gamma radiation from Co^{60} for laboratory experiments involving objects of relatively small size.

An intense and uniform source of γ-rays capable of irradiating large numbers of small specimens was needed in a research program on the thermoluminescence of crystals. A hollow Co^{60} cylinder has solved the problem so successfully that a description of it may be of help to others. Thousands of irradiations have been carried out with this simple and inexpensive source since its development in 1949.[1,2] The γ-ray flux is uniform because of the geometrical characteristics, and it is intense because the samples to be irradiated are placed inside the source and receive radiation from all sides. The γ-radiation extending outward from the source is of sufficiently low enough intensity that safe handling and shipping may be carried out easily. An unshielded 3-curie source giving a radiation intensity of approximately 4 roentgens per hour at a distance of 1.0 meter will provide an intensity of about 6,000 roentgens per hour inside the source.

Similar cylindrical Co^{60} γ-ray sources have been prepared in other laboratories for studies in radiation chemistry[3] and to develop new applications for fission products.[4] The high activity of these other sources (300 to 1,000 curies) requires that special apparatus and techniques be used for safe preparation and handling. The smaller size of the sources described below produces a high radiation intensity per unit of radioactivity, making high γ-ray fluxes available to laboratories not possessing specialized facilities.

A hollow cylinder of cobalt metal powder was prepared by filling the space between two concentric aluminum cans. The aluminum container must be absolutely tight to prevent the escape of any trace of radioactive cobalt powder. The powder was used because it is easily available whereas the machining of cobalt metal is very difficult.[5]

A plan of the apparatus is shown in Fig. 1. The cylindrical aluminum cans were welded from standard aluminum containers used for neutron irradiations in the nuclear reactor at the Argonne National Laboratory. The outer aluminum cylinder has an outer diameter of 3.1 cm. and the inner cylinder has an inner diameter of 2.2 cm. The height is 13.5 cm. The top and bottom of the concentric cylinders are closed with a thick aluminum ring to which the two cylinders are welded after filling up the space between them with pure chemical-grade cobalt powder.

The first model of this apparatus was placed in the nuclear reactor at the Argonne National Laboratory and exposed to a neutron flux for a sufficient time to produce 0.7 curie of radioactive cobalt. Radioactive cobalt (Co^{60}) has a half-life of 5.3 years and decays with the emission of weak β-rays and 1.17 and 1.33 mev. γ-rays.

A second gamma source of the same type was irradiated at the Oak Ridge National Laboratory to produce 3 curies of radioactive cobalt.

Specimens are placed in an aluminum rack which fits in the source. This rack holds several solid pieces, 1 cm. square and a few millimeters thick, sawed from a rock or cleaved from a crystal, or it can hold 40–50 gelatine capsules containing powdered specimens. It has been used for irradiating biological material including live bumble bees and fruit flies. The 0.7-curie and 3-curie irradiators are kept in separate compartments of a lead container with walls seven inches thick. This is set in the floor of an isolated basement room. A mirror is placed at an angle of 45 degrees about 1.0 meter above the irradiators. The specimens are lowered into the irradiator and removed with a "fish pole."

The relative and absolute radiation intensities in the irradiators were determined by using the thermoluminescence of lithium fluoride crystals as dosimeters as will be described in detail in a forthcoming communication. Lithium fluoride, as well as other alkali halides, emits light on heating after an exposure to high energy radiation such as X-rays, γ-rays and α- or β-particles. This thermoluminescence is measured by recording the changes in light intensity as measured by a multiplier phototube while the temperature of the specimen is increased at a rate of about 1° per second. The resulting light intensity–time curve or the

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(1) Farrington Daniels and D. F. Saunders, *Science*, **111**, 462 (1950).

(2) D. F. Saunders, Ph.D. Thesis, University of Wisconsin (1950).

(3) J. A. Ghormley and C. J. Hochanadel, *Rev. Sci. Instruments*, **22**, 473 (1951).

(4) B. Manowitz, *Nucleonics*, **9**, No. 2, 10 (1951).

(5) It has been learned that cylinders of cobalt metal can be made by Technical Fabrications Co., Cambridge, Massachusetts, and by Eldorado Mining and Refining (1944) Ltd. Ottawa, Canada.