times, of leaks at the joints and stopcocks of an order of magnitude less than the rate of transport, of consistent avoidance of contaminations of the order of 10^{-5} molar in small volumes of solution where even the usual CO_2 content of distilled water is fatal, or of adiabatic heating and cooling during pressure change. Other difficulties could be traced to two more basic problems: One is the flexibility and hysteresis of the membrane and its somewhat flexible support by the filter paper. Hence any change of pressure produces a bulk flow as the membrane stretches or contracts and this is followed by further slow motion until a mechanical equilibrium is reached. The other major difficulty lies in temperature control. It should be remembered that a 10^{-4}° temperature difference between the two surfaces corresponds to an error of 8.2 mbar in the osmotic pressure, *i.e.*, over 50% of our equilibrium value as indicated by eq. 6. It was hoped that the close proximity and good thermal contact between the two surfaces would prevent minor temperature fluctuations or drifts from influencing our results. We used finally either an air-bath, whose short range fluctuations were not visible on a tapped Beckmann thermometer, and long-time drift amounted to a few thousandths degree or a water-bath whose variations could not be observed on a tapped Beckmann thermometer. While these gave better results than less elaborate thermostatting, they still seemed insufficient.

The Rate of Transport.—When steady values were obtained, it was often possible to compute the rate of transport as a function of the difference between the applied pressure and the equilibrium pressure. This was reasonably reproducible and of the order of 0.8 mm. hr.$^{-1}$ mbar^{-1}, *i.e.*, about ten times higher than the rate of transport computed above. This difference cannot be accounted for by a heat conductivity greater than assumed. Even if thermal resistance were zero, the rate determined by diffusion alone becomes only 0.12 mm. hr.$^{-1}$ mbar.$^{-1}$. It cannot be due to a reduction of the apparent thickness of the membrane due to the curvature of the menisci since this can amount only to one diameter, which is only $^1/_{300}$ of the thickness. It would also be unlikely that the liquid should penetrate the membrane for even 50% of its thickness over most of its area without causing a leak at some point. Finally, the high rate cannot be due to a leak because a leak causing a tenfold acceleration also would reduce the measured osmotic pressure to one-tenth of the calculated one and this was emphatically not the case in our experiments. Hence an additional vapor phase transport mechanism, such as convection, which appears unlikely, or perhaps surface diffusion, seems to be operating in our membranes.

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ABSORPTION SPECTRA OF OXYGEN AND NITRIC OXIDE IN SOLUTION

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It has become evident recently that some oxygen containing liquids in the ultraviolet region are not inert spectroscopic solvents as was formerly believed. Spectrophotometric investigations of oxygen solutions in aromatic[1] and aliphatic hydrocarbons[1,2] as well as in water[3] recently were reported. Oxygen dissolved in aromatic solvents leads to the enhancement of singlet-triplet transitions[4–7] superimposed on a continuous absorption, which was assigned to a charge transfer transition.[1]

After the present work was completed the intensive study of the interaction of oxygen with organic solvents was published.[8]

Our results are in complete agreement with the conclusions of Tsubomura and Mulliken.

Experimental

Materials and Gases.—Benzene, methanol and ethanol of Analar grade and acetonitrile of Eastman "spectro" grade were used. The alcohols were purified by refluxing with diphenylhydrazine and magnesium metal and finally distilled from calcium oxide. The water was triply distilled. Nitric oxide gas was purified of all traces of nitrogen dioxide by bubbling through sodium hydroxide solution and dried by passing over calcium oxide. Nitrogen was freed from traces of oxygen by passing through a copper-asbestos column at 400°. Oxygen, nitrogen and hydrogen were freed from soluble impurities by bubbling the gases through a trap containing the solvent.

Spectrophotometric measurements were carried out using a Beckman DU Spectrophotometer equipped with an IP 21 photomultiplier, and with a Hilger Uvispek Spectrophotometer. One and 10 cm. absorption cells were used. The absorption cells were equipped with attachments for gas bubbling and for evacuation on a vacuum line. Optical densities were measured against air as a reference.

Procedure.—Solutions were prepared by saturating the liquids for two hours with the appropriate gas at 25°. The absorption spectra of these solutions were measured in the following order: (a) air saturated; (b) nitrogen saturated; (c) oxygen saturated; (d) nitrogen or hydrogen saturated. Nitric oxide solutions were prepared by evacuation of the solvent on a vacuum line through a liquid air trap, followed by saturation of the solution with the gas. During the evacuation and the saturation process the solution was stirred continuously with a magnetic stirrer. Oxygen solutions containing varying gas concentrations were prepared by the same method.

Results and Discussion

Absorption Spectra of Oxygen Solutions.—Oxygen solutions in methanol and ethanol in the ultraviolet region gave rise to a continuous absorption. Similar results were obtained for benzene and water in agreement with previous work.[1–4] A weak absorption of oxygen in acetonitrile could be detected only in a 10 cm. cell. The optical absorp-

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(7) J. N. Murrell, *ibid.*, **3**, 319 (1960).

(8) H. Tsubomura and R. S. Mulliken, *J. Am. Chem. Soc.*, **82**, 5966 (1960).

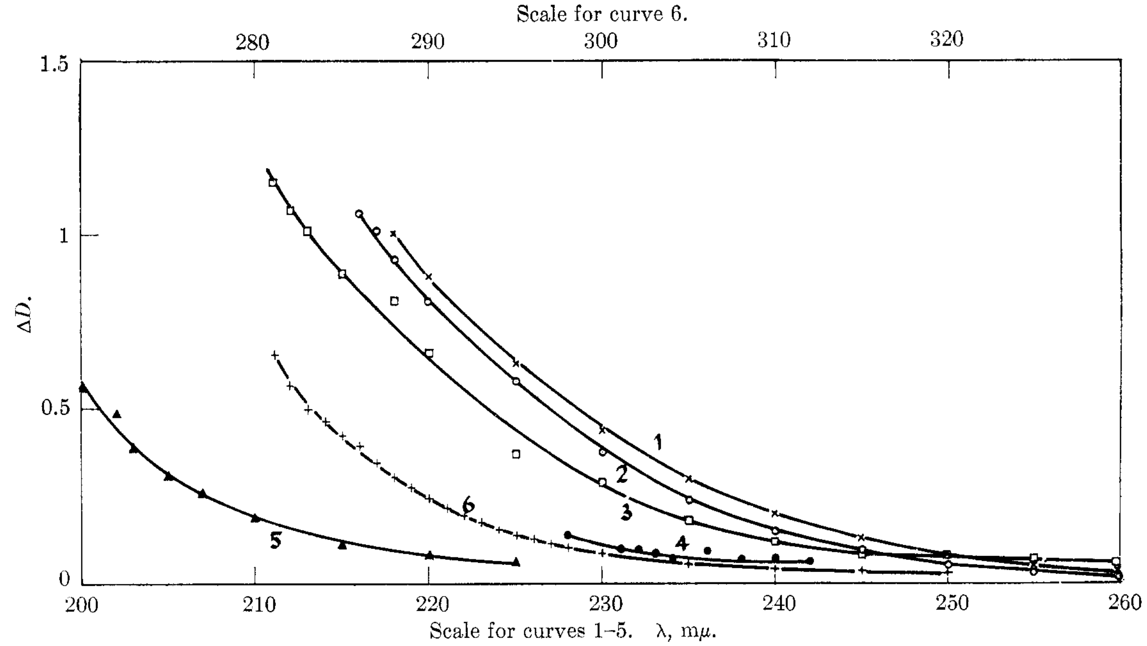

Fig. 1.—Absorption spectra of oxygen and nitric oxide solutions at 25°.

		P, mm.	10^3C, M	$\lambda(\epsilon = 10)$, mμ	Optical cell length, cm.
1	O_2 in methanol	540	7.2	248	1
2	O_2 in ethanol	630	8.1	251	1
3	NO in methanol	214	3.3		1
4	O_2 in acetonitrile	600		<228	10
5	O_2 in water	670	1.12	215	10
6	O_2 in benzene	630	7.7	301	1

tion disappeared on removing the dissolved oxygen by saturation with nitrogen or hydrogen or by evacuation.

The contribution of the dissolved oxygen to the optical absorption was obtained from: $\Delta D = D - D_0$, where D_0 is the optical density of the oxygen-free solution. The apparent molar absorption coefficient of oxygen at 25° was obtained from $\epsilon = \Delta D/C$, where C is the concentration of oxygen calculated from the solubility data.[9] These absorption spectra are presented in Fig. 1. The band maxima could not be determined in the region under investigation. This difficulty is due to the overlap of the continuous band with the absorption of the solvent.

The dependence of ΔD on oxygen concentration was investigated in methanol and ethanol solutions saturated with oxygen. The partial pressure of oxygen was varied in the region 50–500 mm. ΔD was found to vary linearly with the oxygen pressure.

Absorption Spectrum of NO in Methanol.—An absorption band of nitric oxide in methanol was obtained below 260 mμ (Fig. 1). No optical absorption of gaseous nitric oxide at a pressure of 1 atm. in a 1 cm. cell in the region 300–220 mμ was observed. The continuous absorption band of nitric oxide in methanol was found to be shifted toward longer wave lengths compared to the oxygen absorption band. A linear dependence of ΔD on NO concentration was observed.

Nature of the Optical Absorption.—The absorption spectra observed under these conditions are diffusive and no fine structure could be detected. The molar absorption coefficients for oxygen and nitric oxide solutions are about 10^2 higher than the singlet–triplet transitions of liquid benzene enhanced by O_2[5] and by NO.[6] Thus it appears that these bands are not due to singlet–triplet transitions of the solvent molecules. The marked dependence of the absorption band on the solvent clearly indicates that the absorption is not due to the forbidden $^3\Sigma^- \rightarrow {}^3\Sigma_u^+$ transition of the dissolved oxygen.

Following previous suggestions[1,8,10,11] these continuous bands are assigned to charge transfer spectra of oxygen and nitric oxide. The electron affinity of O_2 based on thermochemical data is of the order of 0.7–1 e.v.,[12,13] while the electron affinity of NO is positive.[12] Thus these molecules may act as electron acceptors in an electron transfer process.[14] A support for this conclusion in the case of oxygen is obtained by considering the relation between the energy associated with the optical process and the ionization potential of the solvent molecule. As the maxima of these absorption bands could not be determined, the band onset energies $h\nu_0$ were chosen. For the solvents experimentally investigated we chose arbitrarily $\epsilon = 10$ as the band onset. It is thus assumed that the vibrational broadening is independent of the nature of the electron donor. For the iodine charge transfer complexes the energy difference

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(9) A. Seidel, "Solubilities of Inorganic and Organic Compounds," D. Van Nostrand Co., New York, N. Y., 1940.

(10) D. F. Evans, *J. Chem. Phys.*, **23**, 1424 (1955).

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U between band maximum and band onset energies remains constant within 0.2 e.v. In Fig. 2 the linear plot of $h\nu_0$ against the ionization potential for oxygen solutions is presented over a somewhat more extended region than was recently given.[8] The band onset of acetonitrile is located at $\lambda <$ 228 mμ, $h\nu_0 >$ 126 kcal., which is consistent with the high ionization potential 12.2 e.v.[15] of this molecule. This linear plot is a straightforward result of Mulliken's[14,16] theory.

Considering the quantitative relation between the charge transfer absorption and ionization potential, Mulliken's theory leads to the result[16]: $h\nu_0 = I - E + W + 2\beta^2/(I - E + W) - U$ where I is the vertical ionization potential of the electron donor, E is the vertical electron affinity of oxygen, W the stabilization energy of the excited state in the nuclear configuration corresponding to the ground state and β the resonance integral.

For extremely weak complexes $\beta^2 << I - E + W$ and no deviation from linearity[16] should be expected. The slope obtained from Fig. 2 is 0.65. This deviation of the slope from unity may be due to the dependence of W on I[17]; however, the data are not accurate enough to establish these points.

Analysis of Solubility Data of O_2.—The pronounced temperature effect on ΔH for the solubility of oxygen in water was explained[3] as being caused by the formation of two distinct species involving hydrated oxygen. However, a similar temperature dependence of ΔH was observed for the rare gases, nitrogen and hydrogen dissolved in water.[18] As was shown by Eley[18] this behavior is due to the temperature effect on the energy and entropy changes associated with the breaking of the water structure and the formation of cavities in this liquid.

From the solubility data of oxygen in methanol,[9] ethanol[9] and benzene[19] linear plots of log β (β-Ostwald solubility coefficient) against $1/T$ were obtained over a wide temperature region. For these solvents, in variance with the properties of aqueous solutions ΔH for the solubility of oxygen is temperature independent. In the case of organic solvents the temperature effects on the heats and entropies of solubilities should be much smaller.[20]

These results indicate the lack of thermochemical evidence for consecutive complex formation in oxygen solutions. The temperature effect on the absorption bands of oxygen in water[4] may be due to the effect of the increase of the amplitude of thermal vibrations leading to temperature broadening of the band threshold.

The numerical values for heats of solution of oxygen in water and in benzene are of the same order of magnitude within 0.5 kcal. as for other gases of comparable size and polarizability.

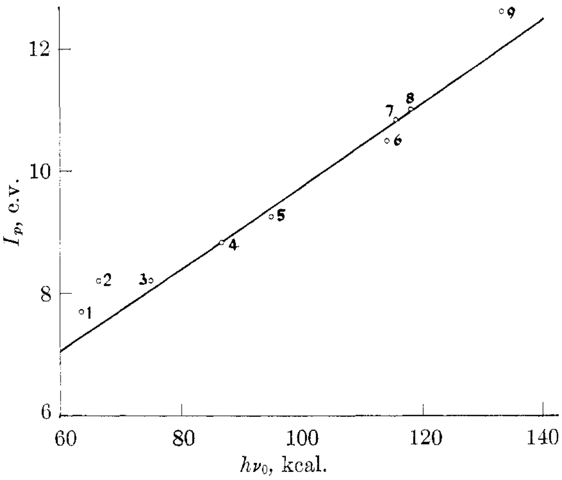

Fig. 2.—The dependence of the equivalent energy of the charge transfer band onset on the ionization energy of the solvent molecule; ionization potentials from K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1952) and ref. 16: (1) aniline[1]; (2) pyrrole[1]; (3) anisole[1]; (4) toluene[1]; (5) benzene; (6) ethanol; (7) methanol; (8) cyclohexane[2]; (9) water.

The solubility data of oxygen, nitrogen and argon were compared.

For water at 4°

$$\Delta H(O_2) = 3.9 \text{ kcal. mole}^{-1}\ {}^{4}$$
$$\Delta H(A) = 3.73 \text{ kcal. mole}^{-1}\ {}^{18}$$

For benzene at 20°

$$\Delta H(O_2) = 0.36 \text{ kcal. mole}^{-1}$$
$$\Delta H(N_2) = 0.86 \text{ kcal. mole}^{-1}$$

and

$$\Delta H(A) = 0.82 \text{ kcal. mole}^{-1}\ {}^{21}$$

It thus appears that there is no thermochemical evidence for complex formation in these solutions. As was suggested recently[8] these continuous absorption bands of oxygen and nitric oxide probably are the result of a contact charge transfer[22] process.

[15] K. Watanabe and T. Nakayama, "Technical Report No. 1," University of Hawaii, 1958.

[16] S. H. Hastings, J. L. Franklin, J. C. Schiller and F. A. Matsen, *J. Am. Chem. Soc.*, **75**, 2900 (1953).

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[22] L. E. Orgel and R. S. Mulliken, *J. Am. Chem. Soc.*, **79**, 4389 (1957).

POTENTIAL DETERMINING IONS AND THE COAGULATION VALUE

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In a paper by Kratohvil, Orhanović and Matijević[1] the problem of dependence of the coagulation concentration of the potential determining, constituent and stabilizing ions was brought forward and the role of Bjerrum's distance in the coagulation discussed.

The dependence of the coagulation value of the potential determining ion was in the majority of papers of this school (ref. 1 and the cited literature) represented by plots "logarithm coagulation concentration (value) against logarithm total concen-

[1] J. P. Kratohvil, M. Orhanović and E. Matijević, *J. Phys. Chem.*, **64**, 1216 (1960).