

Letters to the Editor

THIS section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge (\$3.00 per page) will not be made and no reprints will be furnished free.

Isotopic Exchange Between Carbon Tetrabromide and Bromine

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WEIGHED quantities of carbon tetrabromide and of bromine containing radioactive isotopes were allowed to react in Pyrex vessels of sufficient size to permit complete volatilization of the reactants. The radioactive bromine was obtained by exposing bromoform to neutrons from the cyclotron; it was allowed to age for periods of about 24 hr. to allow for decay of the two isotopes of shorter life.¹ The activity of the samples was measured with a Lauritsen electroscopes. The rate of exchange of radioactive bromine could be determined conveniently over the temperature range 170° to 200°C. Molar concentrations of carbon tetrabromide and bromine were varied from a ratio of 10 : 1 to a ratio of 1 : 10. The reaction appears to be homogeneous, and the rate appears to be directly proportional to the concentration of the carbon tetrabromide and to the square root of the concentration of the bromine. This indicates a mechanism involving bromine atoms. If it is assumed that exchange occurs between a carbon tetrabromide molecule and a bromine atom, the energy of activation of this bimolecular process is zero. This is obtained by plotting $\log [(measured\ exchange\ rate)/(CBr_4)(Br)]$ against $1/T$. The value of (Br) is calculated from the equilibrium constant of the reaction $Br_2(g) \rightleftharpoons 2Br(g)$.

The same procedures were repeated using Pyrex capsules of small capacity in order to maintain the reactants in the liquid phase. The exchange rate was measured over the temperature range 107° to 160°C. The mechanism of the reaction seems to be the same as that in the gaseous phase. In this case, however, there is an energy of activation of about 3 kcal. The values of the activation energies for the reaction in the gaseous and liquid phases may be somewhat in error, first because of the extrapolation of the equilibrium constant expression to the rather low temperatures of our experiments, and second because of the inherent limits of accuracy in our experimental technique. An additional small error is involved in the use of this same equation in calculating the degree of dissociation in the liquid phase.

No parallelism can be detected between the intensity of the radioactivity of the bromine sample and the value of the specific reaction rate calculated for the runs. Furthermore, no exchange occurs at room temperature. These facts seem to indicate a thermal reaction and not one initiated by the energy of the nuclear decomposition.²

Calculation of theoretical rates on the basis of the collision theory, assuming a bimolecular reaction between carbon tetrabromide molecules and bromine atoms gives values in both the gaseous and liquid phases which are too large by a factor of between 10^4 and 10^6 .

¹ Willard, J. Am. Chem. Soc. **62**, 256 (1940).
² Liberatore and Wiig, J. Chem. Phys. **8**, 165, 349 (1940); Libby, *ibid.* **8**, 348 (1940).

Infra-Red Absorption Spectrum of Acetone

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THE infra-red spectrum, from 3–20 μ , of gaseous acetone was obtained with a spectrometer¹ using fluorite, rocksalt, and KBr prisms. The acetone used was Mallinckrodt C.P. which had been refluxed and redistilled in this laboratory.

The spectra obtained for the three prisms are shown in Fig. 1. There is, though this is not evident in the figure, a shoulder on the low frequency side of the 1363 band. The frequencies and their qualitative intensities are given in

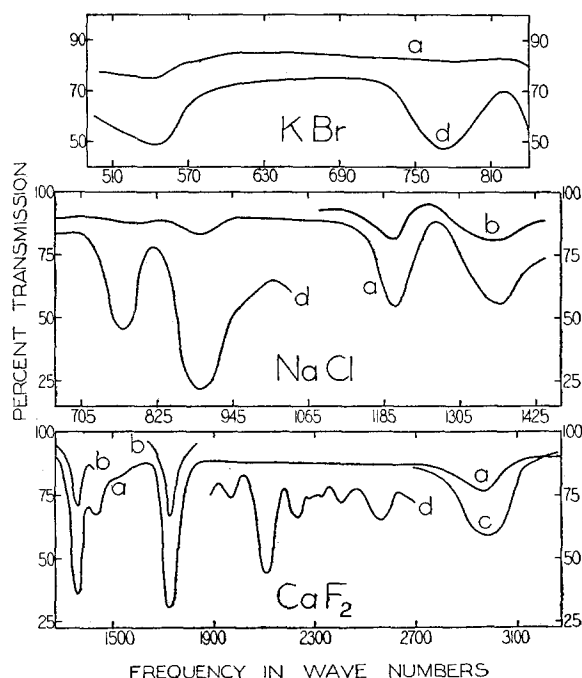


FIG. 1. The infra-red absorption spectrum of acetone gas. The transmission curves were taken in a 30-cm glass cell using NaCl windows with gas at the following pressures: a, 5 mm; b, 1.1 mm; c, 16 mm; d, 200 mm.

TABLE I. The infra-red spectrum of acetone gas.

FREQUENCY IN CM ⁻¹	INTENSITY	FREQUENCY	INTENSITY
547	medium	1964	weak
774	medium	2109	medium
896	strong	2234	weak
1202	740 cm ⁻¹	2418	weak
1363	1007 cm ⁻¹	2554	weak
1430	strong	2984	strong
1725	1552 cm ⁻¹		

Table I. By use of Wells' method,² the intensities of the three strongest bands were computed for $p=100$ mm. These results are the numerical values for the 1202, 1363, and 1725 bands given in Table I. It was assumed that acetone was at least as complicated as propylene, and hence no dilution with an inert gas was necessary. Moreover, the region 1.1–5 mm of the curve, $\ln(D_0/D)$ vs. p , was assumed practically a straight line. Wells' curves seem to justify this, but since only two points were taken and these determined by graphical integration, the values are given only as semi-quantitative approximations. Corrections were made for the blanks, but the stray effect was considered negligible in this region.

No other data are available for the vapor, but Coblenz obtained the infra-red absorption spectrum for liquid acetone, and Edsall and Wilson³ have obtained the most recent Raman spectrum.

¹ H. Gershinowitz and E. B. Wilson, Jr., *J. Chem. Phys.* **6**, 197 (1938); E. B. Wilson, Jr., and A. J. Wells, *J. Chem. Phys.* **9**, 319 (1941).
² A. J. Wells, thesis, Harvard University, Cambridge, Massachusetts (1941); E. B. Wilson and A. J. Wells, *J. Chem. Phys.* **9**, 659 (1941).
³ J. T. Edsall and E. B. Wilson, Jr., *J. Chem. Phys.* **6**, 124 (1938).

The Exchange Reaction Between Gaseous and Combined Nitrogen

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USING radioactive nitrogen (N^{15}) as an indicator, Nishina, *et al.*¹ have reported that N_2 gas undergoes rapid exchange at room temperature with dilute (0.1–0.2M) solutions of $NaNO_3$, $NaNO_2$, $NH_2OH \cdot HCl$, etc. Moreover, according to these authors, the rate of exchange decreased with increasing concentration of nitrate or nitrite. Since these results are both unexpected and at variance with other investigations,^{2,3} it has been considered desirable to repeat the experiments.

Charcoal was bombarded in a gas-tight chamber (containing 100 cc tank N_2) with 30μ of 8-Mev deuterons. Under these conditions ~30 percent of radioactive nitrogen formed⁴ is present in gaseous state. An appreciable fraction of the gaseous activity is present as combined nitrogen² (formed by the recoiling N^{15} as a result of deuteron impact). Since the presence of combined nitrogen "impurity" can be construed as evidence for exchange, it is important to remove it from the labeled N_2 . To this end the gaseous activity was pumped out of the target chamber and mixed with carrier (inactive) HCN and NO_2 . The mixture was

slowly pumped through a heated combustion tube containing CuO and was then passed through three glass spirals immersed in liquid air. By means of two Töpler pumps, one at each end of the train, the gas was forced back and forth several times through the CuO and cold traps.

After this treatment two portions of ~50 cc of the N_2^* were vigorously shaken for ten minutes with 10 cc $NaNO_3$ and 10 cc $NaNO_2$ solution in separate (previously evacuated) vessels. The solutions were then gently boiled to drive off dissolved N_2 and were analyzed for radioactivity using methods described elsewhere.⁵ The results are summarized in Table I.

TABLE I.

SUBSTANCE TESTED	CONCENTRATION (MOLES/LITER)	RADIOACTIVITY ^a (COUNTS/MINUTE)
$NaNO_3$	1.2	<4
	.1	<4
$NaNO_2$	1.3	<3
	.1	<5

^a All figures are corrected for decay of N^{15} to the time of counting the first sample and are therefore comparable. The N_2^* had an activity of 10^5 counts/minute.

It is apparent from Table I that <0.01 percent of the N_2^* has exchanged with NO_3^- or NO_2^- . This is in agreement with the results of Burris and Miller³ on N_2 fixation by *Azobacter* using heavy (N^{15}) nitrogen gas.

¹ Nishina, Iimori, Kubo, and Nakayama, *J. Chem. Phys.* **9**, 571 (1941).

² Ruben, Hassid, and Kamen, *Science* **91**, 578 (1940).

³ Burris and Miller, *Science* **93**, 114 (1941).

⁴ The remainder can be removed by completely burning the charcoal to carbon dioxide. This was not undertaken due to the short half-life of N^{15} (10.5 minutes).

⁵ Ruben, Kamen, and Hassid, *J. Am. Chem. Soc.* **62**, 3443 (1940).

Measurement of Tension in Solutions

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ALTHOUGH many properties of solutions have been studied, there appears to be no record of any systematic study of the maximum hydrostatic tension which solutions can withstand under varying conditions of temperature and concentration. With the publication of Vincent's ingenious method for measuring this tension such a study seemed possible and we have accordingly undertaken it in the hope of obtaining information of value to the problem of the structure of solutions. This letter is a preliminary report on the first experiments of this project.

Vincent's apparatus can be described briefly. It consists of a metallic bellows, closed by a needle valve, which contains the liquid under test. Inward leakage of air into the bellows is eliminated by surrounding the bellows and valve by the same liquid. With the bellows filled and the valve closed a gradually increasing load is applied to the bellows until the liquid breaks. The hydrostatic tension existing