

Interpretation of the Visible Absorption of Bromine

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The Separation of Gases by Diffusion

Classical methods of atmolysis depend either upon reducing the pressure of a gas mixture to be separated to such a point that the mean free path of the molecules assumes macroscopic dimensions, as in a diffusion pump, or by use of solid septa having passages of the order of magnitude of intermolecular dimensions at ordinary pressures, so that gas molecules may pass through them relatively free from collision with other gaseous molecules. Either method results in capacities that are infinitesimal, based on the volume of gas treated as measured under normal conditions.

For the past several years, work of a technical nature has been going on at the Pacific Experiment Station of the Bureau of Mines, U. S. Department of the Interior, to separate gases of different molecular weights by diffusion at normal pressures, and this work has been highly successful. Separations comparable to the perfect functioning of Graham's law, no matter what the initial composition of gas treated, have been shown possible at rates that are enormous when compared to the classical methods, or to the recently much investigated methods of thermal diffusion.

The method used is extremely simple and is based upon the realization that if the constituents of a binary mixed gas diffuse into a third gas, the relative rate of diffusion of the constituents will in general be close to the Graham's law ratio. We have made the third gas steam, or any condensible vapor, provided a short diffusion path, and attached a regulating valve and two condensers to the atmolyzer unit.

The device is in essence a diffusion boundary, whose only purpose is a hydrodynamical one of separating the flow of two streams of fluid contiguous to one another. The apertures connecting the streams may be of any convenient size, a suitable screen being ordinary perforated sheet brass, 26 gage, 625 perforation per sq. in., each perforation nominally $\frac{1}{16}$ in. diameter. Steam is made to flow uniformly along one side of such a boundary, which may be conveniently cylindrical, and the gas to be separated is caused to flow countercurrently along the opposite side. A throttle valve in the steam line adjusts the static pressures on opposite sides of the boundary to a close approximation of balance, and under these conditions the stream of gas is divided into two fractions, in proportions that are changed at will by adjustment of the valve, whereupon the gas issuing into the steam duct will be found after condensation of vapor to be greatly enriched. The lesser the fraction diffusing into the vapor stream, the lower the extraction and the greater the ratio of concentration. Using a flow of vapor sufficiently great, back diffusion is prevented, and a maximum constant concentration gradient maintained.

The imposition of a mass motion upon the diffusive flow, per or contra, enables all degrees of ratio of concentration to be obtained, exceeding those given by Graham's law for a condition in static pressure balance.

Some idea of the effectiveness of this method may be gained from the following approximate performance under conditions technically interesting for the separation of hydrogen from nitrogen or carbon monoxide: (1) Original gas 30 percent hydrogen, in one pass produces 55-65 per-

cent product with an extraction of 75-85 percent. (2) Second pass produces 75-85 percent product, with similar yield. (3) Third step produces gas better than 98 percent H_2 . (4) Area of diffusion boundary 60-75 sq. cm. (5) Capacity 0.5 to 1.0 liter per minute of product. (6) Steam consumption approximately 2-3 grams per liter of product per stage. (7) Operating temperature 135-150°C, pressure near atmospheric.

The writer has been interested primarily in the many possible technical applications of such methods. He commends it to the attention of those interested in isotopes, a subject he is unable to develop himself. The methods and apparatus are the subject of a patent application, assigned to the U. S. Secretary of the Interior for administration in public interest, and the process may presumably be licensed without cost. A bulletin describing the results of more than 3000 tests of various types of diffusion boundaries is in course of preparation and will discuss in detail the theory and practise of technical atmolysis by this method.

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July 17, 1939.

Interpretation of the Visible Absorption of Bromine

Recent work on the visible bromine continuum in solution^{1,2} together with data from Brown³ and Darbyshire,⁴ can be used to decide between Mulliken's alternative interpretations⁵ of the *A* and *B* components,⁶ namely—

$$\begin{array}{l} A \quad \begin{cases} {}^1\Pi_u \leftarrow {}^1\Sigma_g^+ \\ {}^3\Pi_{0+u} \leftarrow {}^1\Sigma_g^+ \end{cases} \\ B \quad \begin{cases} {}^3\Pi_{1u} \leftarrow {}^1\Sigma_g^+ \end{cases} \\ \text{Coupling—}\Omega-s. \end{array} \quad (1)$$

and

$$\begin{array}{l} A \quad \begin{cases} {}^1\Pi_u \leftarrow {}^1\Sigma_g^+ \\ {}^3\Pi_{0+u} \leftarrow {}^1\Sigma_g^+ \end{cases} \\ B \quad \begin{cases} {}^3\Pi_{1u} \leftarrow {}^1\Sigma_g^+ \end{cases} \\ \text{Coupling—}\Lambda-\Sigma. \end{array} \quad (2)$$

Although (2) has been established for chlorine,⁷ Mulliken suggests that (1) is more probable for the comparatively heavy bromine molecule.

Since the perturbations due to neighboring solvent molecules will cause the further breakdown of selection rules that are already violated in the gas, (2) would mean that solvents should enhance the *B* component more than *A*, since *B* would contain the "forbidden" intersystem transitions, Σ being a good quantum number. This is opposed to the experimental data, which show *B* to be affected but little, while *A* is increased some 30 percent. With $\Omega-s$ coupling (1), however, Σ is no longer a good quantum number and intersystem transitions should not be enhanced by perturbations. In this case, the only violation of a selection rule is that of $\Delta\Omega_c = \Delta\Lambda_c$ by ${}^3\Pi_{0+u} \leftarrow {}^1\Sigma_g^+$, occurring in the *A* continuum which experiment shows to be enhanced.

Bayliss⁸ and Darbyshire⁴ have produced Franck-Condon evidence in favor of (2), including the correspondence of the $U'(r)$ curve calculated from the *B* continuum with the Morse curve calculated from the band data on ${}^3\Pi_{0+u}$. Since (2) requires the $U'(r)$ curve for *B* to be an average of two,

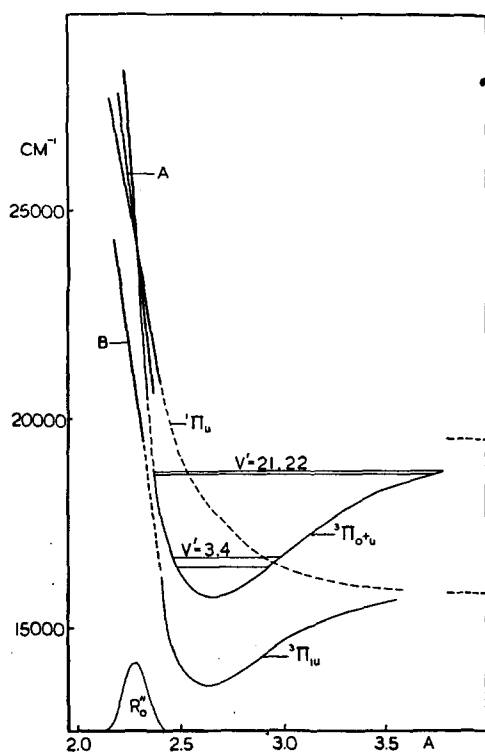


FIG. 1. Potential energy—nuclear separation curves for bromine. Curves marked A and B are calculated from the continuum.

and since Morse curves are generally incorrect for high v' , this correspondence is probably fortuitous. On interpretation (1), the calculated $U'(r)$ curve for A must be an average curve, and theoretical work on the effect of solvents makes it appear that it consists of two components crossing at approximately $24,000\text{ cm}^{-1}$. Unpublished theoretical considerations have shown that, in associated solvents such as water, the $U''(r)$ curve for $^3\Sigma_g^+$ is displaced to slightly smaller r'' values. In the case of water, it is required to displace the v_0'' eigenfunction some 0.02 Å to smaller r'' values. In such a case, the two $U'(r)$ curves crossing at $24,000\text{ cm}^{-1}$ would cause the two superimposed maxima in component A to separate, leading to a broadening of the A continuum with little change in ϵ_{max} , as is observed. This is borne out by the fact that the integrated intensity is approximately the same as in other solvents.

The $U(r)$ curves for the various states have been constructed in a semi-quantitative way and are illustrated in the accompanying Fig. 1. The $U'(r)$ curve for B extrapolates reasonably to the Morse curve for $^3\Pi_{1u}$, obtained by Darbyshire on what he considers to be the most probable numeration. Such a system of $U(r)$ curves requires $^1\Pi_u$ to cross $^3\Pi_{0+u}$ at about $16,500\text{ cm}^{-1}$ and $^3\Pi_{1u}$ to approach $^3\Pi_{0+u}$ very closely at about $18,700\text{ cm}^{-1}$, at both of which points perturbations in the vibrational levels of the $^3\Pi_{0+u}$ state should occur. It is significant that Darbyshire⁴ observed anomalies which led him to conclude that the $v'=3$ and 4 levels of $^3\Pi_{0+u}$ were perturbed and that these vibrational levels lie close to $16,500\text{ cm}^{-1}$; and also that

Brown³ observed a change in the law of force for vibrations in the region of the levels $v'=21$ and 22 for the same $^3\Pi_{0+u}$ state, that is, at about $18,700\text{ cm}^{-1}$.

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University of Western Australia,
June 30, 1939.

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² Child and Walker, Trans. Faraday Soc. **34**, 1506 (1938).

³ Brown, Phys. Rev. **39**, 777 (1932).

⁴ Darbyshire, Proc. Roy. Soc. London **A159**, 93 (1937).

⁵ Mulliken, J. Chem. Phys. **4**, 620 (1936).

⁶ Acton, Aickin and Bayliss, J. Chem. Phys. **4**, 474 (1936).

⁷ Aickin and Bayliss, Trans. Faraday Soc. **33**, 1333 (1937).

⁸ Bayliss, Proc. Roy. Soc. London **A158**, 551 (1937).

Fluorescence of Glyoxal Vapor

Matheson and Zabor* have described in this journal some measurements on the fluorescence of certain aldehydes and ketones, the similarity of which to each other suggests that a common product of photolysis is responsible for the fluorescence. Although both experimentally and otherwise I am in agreement with their conclusions, it may be of interest to report measurements on the fluorescence of another dialdehyde, glyoxal vapor, which indicate a different mechanism for the fluorescence in this case. This result might have been expected since the glyoxal molecule contains no methyl groups. Glyoxal vapor shows two systems of absorption in the near ultraviolet, namely *ca.* $4600\text{--}3400\text{ Å}$ and *ca.* $3200\text{--}2300\text{ Å}$, respectively. The bands of the former region have been studied under low dispersion and in the third order of a 21-foot grating, and reveal a system of discrete bands with remarkably fine structure; the other absorption region to higher frequencies appears to be composed of diffuse (predissociated) bands. With a view to obtaining help in the vibrational and rotational analysis of the discrete band system, the fluorescence of the vapor has been photographed, by using as exciting frequencies the lines emitted by a mercury vapor lamp $3600\text{--}4400\text{ Å}$, and a glass prism spectrograph of high aperture and resolving power, having a dispersion of about 40 Å per mm at 4400 Å . A well-marked system of sharp bands is observed in fluorescence between $4200\text{--}5200\text{ Å}$, the strongest bands being in the blue-green, and particularly that at *ca.* 4780 Å . This band system is unlike the fluorescence emission spectrum of any other simple aldehyde or ketone, and in particular may be contrasted in both spectral region and structure with that shown by formaldehyde when the latter molecule is irradiated with ultraviolet frequencies. It is hoped shortly to suggest a detailed vibrational analysis of the fluorescence spectrum together with a partial analysis of some of the absorption bands. Although the latter appear to be very complicated, the nature of the fine structure of certain bands suggests that the moments of inertia of the molecule are such that the molecule must exist in the *trans*-form, which has also been considered in the case of the electronically closely related molecule butadiene $\text{CH}_2 : \text{CH} : \text{CH} : \text{CH}_2$.

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August 3, 1939.

* Matheson and Zabor, J. Chem. Phys. **7**, 536 (1939).