Remarks on Mizushima's Method for the Determination of Surface Area of Powders

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Hydrogen peroxide containing 10 percent by weight of water was obtained from the Buffalo Electrochemical Company. It was further purified and concentrated by vacuum distillation. Deuterium peroxide was prepared by the method of Feher,[3] the amount of hydrogen present in the final sample being estimated at 8 to 10 percent of the deuterium content based on a comparison of band intensities. The spectra were obtained with a Perkin-Elmer Model 12B which had been modified into a double beam instrument recording directly the percent transmission; a fluorite, rock salt or potassium bromide prism was used depending on the region. The cell used has been described by Wagner and Hornig,[4] the sample being contained in a small silver chloride holder which provided a fixed film thickness of about 15 microns. At the temperatures employed, decomposition during the course of two or three hours was small.

The bands observed for supercooled liquid hydrogen peroxide (99.2 percent) and liquid deuterium peroxide (82.5 percent) at $-30°C$ and for crystalline hydrogen peroxide at $-30°$ and $-78°$ are listed in Table I. The low frequency band noted by Giguère

FIG. 1a. Low frequency bands.

FIG. 1b. The OH region.

TABLE I. Infra-red frequencies of hydrogen and deuterium peroxides.

H₂O₂ Liq., $-30°$	Cryst., $-30°$	D₂O₂ Cryst., $-78°$	Liq., $-30°$	Sym-metry	Assign-ment
635 m, br		472 vw 660 s 792 w	538 m, br		$\nu_4(?)$
878 vw		878 vw	878 vw	a	ν_3
1353 ms	1365 s	1378 s	1004 s (1386 w)	b	ν_6
	1418 w	1430 w		a	ν_2
2796 mw, br	2743 m	2733 m	2087 mw		$\nu_3+\nu_6(?)$
3360* vs	3275* vs	3218 vs	2482 vs (3368 mw)	b b	ν_5
4715 vw	4640 vw	4595 vw		A	$\nu_5+\nu_6$

* Obtained by difference from the combination band, ν_5+_6.

was observed in the liquid at $-30°$ as a broad band of moderate intensity with a maximum at 635 cm^{-1}. In the deuterium sample under similar conditions, the maximum appeared at 538 cm^{-1}. The observed ratio of hydrogen to deuterium frequency is thus 1.18, whereas the Teller-Redlich product rule, using the known frequencies[2] of the other vibrations of the same species, predicts a ratio of approximately 1.35 for ν_4, the torsional motion of the OH groups. The spectrum of crystalline hydrogen peroxide at $-78°$ exhibited considerably more detail than the liquid and is shown in Figs. 1a and 1b. Both the intensity and sharpness of the low frequency band increased markedly compared to the liquid and two new bands of low intensity appeared separated from the main maximum by 132 cm^{-1} and 188 cm^{-1} on the high and low frequency sides respectively. The 132 cm^{-1} frequency agrees well with the difference of 135 cm^{-1} found between the main Raman OH band in the crystal and a subsidiary band on its high frequency side[2] and probably can be assigned to a lattice vibration. The spectrum of crystalline deuterium peroxide was not obtained and further experimental work will be necessary to establish conclusively the nature of the band at 660 cm^{-1} in the crystal spectrum.

The unsymmetrical bending mode, ν_6, was also much sharper and more intense in the crystal at $-78°$; the sharp and rather weak band on its high frequency side appears at the position expected for ν_2, the symmetrical bending mode, which is also allowed in the infra-red but which until now has only been observed in the Raman spectrum. The shoulder on the low frequency side appears due to the first overtone of the 660 cm^{-1} band.

The band around 2800 cm^{-1}, on the basis of the above data, cannot be given the assignment proposed by Giguère. The shape and position of the band at 2733 cm^{-1} in the crystal at $-78°$
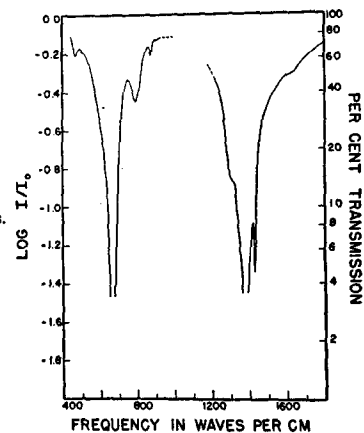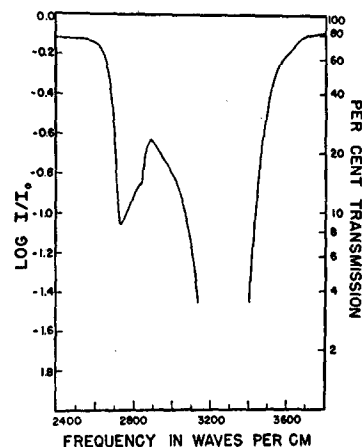
suggest that it is due to the unresolved overtones of the two bending modes, ν_2 and ν_6. However, both fundamentals shift to higher frequencies as the crystal temperature decreases, whereas the 2733 cm^{-1} band shifts slightly to lower. Further work over a wider range of temperatures seems necessary for a more satisfactory answer.

It is hoped that work can be resumed on this problem shortly and a more complete account presented in the fairly near future. The author would like to express his appreciation to Dr. Giguère for making his manuscript available in advance of publication.

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† Dr. Giguère, in a private communication, reports this band now at 610 cm^{-1} at room temperature.
[1] P. A. Giguère, J. Chem. Phys. 18, 88 (1950).
[2] R. C. Taylor, Thesis, Brown University, Providence, R. I. (1947).
[3] F. Feher, Ber. d. d. chem. Ges. 72, 1789 (1939).
[4] E. L. Wagner and D. F. Hornig, J. Chem. Phys. 18, 296 (1950).

Remarks on Mizushima's Method for the Determination of Surface Area of Powders

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RECENTLY Mizushima[1] proposed a method for the determination of surface area of powders using adsorption and adhesion tension data. His method is based on the following

equations:

$$kT \int_1^{n} \ln \frac{p_s}{p(\nu)} d\nu = a(\sigma_s - \sigma_{sl}), \qquad (1)$$

$$a = \frac{kT \int_1^{n} \ln(p_s/p(\nu)) d\nu}{\sigma_{lv} \cos\theta}, \qquad (2)$$

where p_s is the saturation pressure of the liquid, $p(\nu)$ is the vapor pressure at which ν molecules of the vapor are adsorbed by a solid of area a, σ_s, σ_{sl}, and σ_{lv} are respectively the interfacial tensions of the solid-vacuum, solid-liquid, and liquid-vapor interfaces and θ is the contact angle. It is believed the theory is fundamentally unsound and the alleged experimental support non-existent.

Equation (1) was obtained by equating the change of free energy, ΔG, of the adsorbate to the change of the available surface energy of the adsorbent. Since these two effects are entirely different, it is not correct to equate the one to the other to obtain Eq. (1). This can be easily demonstrated when the equations for these energy changes are compared. For a single adsorbate at constant temperature,

$$\Delta G = \int \mu d\nu,$$

where μ is the chemical potential; for the adsorbent,

$$\sum_{\substack{\text{all surface} \\ \text{phases}}} \int a d\sigma = - \int \nu d\mu$$

by the familiar Gibbs' equation. Obviously ΔG cannot be identified with $a(\sigma_s - \sigma_{sl})$ as Mizushima has contended.

The transformation of Eq. (1) into (2) by means of du Pré's equation, $\sigma_{vl} \cos\theta = \sigma_s - \sigma_{sl}$, involves another common misconception. The du Pré equation is strictly an equilibrium relation. If a liquid spontaneously spreads on a solid surface, equilibrium evidently does not exist, and the du Pré equation is no longer valid. In such cases it is not permissible to assume that the contact angle is zero, because spontaneous spreading indicates there is *no* contact angle which is quite different from a zero angle. The system toluene-glass used by Mizushima is precisely such a system to which the du Pré equation cannot be applied, because toluene will spontaneously spread on glass. Even granting that it is permissible to apply the du Pré equation to such systems, Mizushima's fourth equation

$$\sigma_{lv} \cos\theta = 46.5 \text{ ergs/cm}^2$$

is still untenable, because $\sigma_{lv} \cos\theta$ can never be greater than the surface tension of toluene, which is 27.9 at 25°C. Mizushima attributed the above relation to Bartell and Merrill[2] without realizing that these authors have never used $\sigma_{lv} \cos\theta$ to evaluate the adhesion tension of systems like toluene-glass.

In the application of adhesion tension $(A \equiv \sigma_s - \sigma_{sl})$ it should be noted that A depends not only on the nature of the liquid and the solid, but also on the structure of the solid surface. For instance, against the same liquid the (111) plane of NaCl would undoubtedly give different adhesion tension value than the (100) plane. Even with amorphous substances such as charcoal different samples will often give different A values against the same liquid.[3] It is, therefore, erroneous to assume that when equal areas of two solids of the same chemical composition are compared, they will invariably show identical energy effects. In order to test his theory, Mizushima compared the ΔG value calculated from the adsorption data of Carver[4] with the adhesion tension value of Bartell and Merrill and obtained excellent agreement. Carver's data, however, were obtained with Pyrex glass while the adhesion tension value cited (46.5 ergs/cm²) was for fused quartz. There is no reason to expect that two such different solids would show the same surface characteristics. Hence these data are not comparable. It is also to be noted that in the adsorption of vapors by plane surfaces at saturation pressure, the change in surface energy is not $a(\sigma_{sl} - \sigma_s)$ but $a(\sigma_{sl} + \sigma_{lv} - \sigma_s)$, because a liquid surface has been created. This factor has not been considered by the author. Furthermore, it is a well-known fact that cleaning

agents often roughen glass surfaces to such an extent that the effective surface area may be many times greater than the macroscopic geometric value.[5] Since Carver has subjected his glass to quite drastic treatment, it is very probable that the true area is much greater than the value given in his paper. Hence, Mizushima's ΔG value (44 ergs/cm²) may be easily in error by many hundred percent.

From the above discussion the only conclusion which seems justified is that the close agreement of the two energy values obtained by Mizushima only serves to reveal the incorrectness of his theory.

[1] Mizushima, J. Chem. Phys. **17**, 1357 (1949).
[2] Bartell and Merrill, J. Phys. Chem. **36**, 1178 (1932).
[3] Bartell and Smith, Ind. Eng. Chem. **21**, 1102 (1929).
[4] Carver, J. Am. Chem. Soc. **45**, 63 (1923).
[5] Frazer, Patrick, and Smith, J. Phys. Chem. **31**, 897 (1927).

The Stability of Gaseous Nitryl Chloride

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TO date there had been no study of thermodynamic properties of nitryl chloride, $ClNO_2$. However, it appears to be a matter of common belief that nitryl chloride cannot be formed in significant amounts from Cl_2 and N_2O_4, and that it does decompose into these substances.[1] The inferences regarding equilibrium are obvious, and would enable estimation of a rough limit for the standard free energy of formation of $ClNO_2$. In studies aimed at structure analysis we have observed the infra-red absorption spectrum of gaseous $ClNO_2$, prepared both by ozonization[1] of $ClNO$ and by the reaction of chlorosulfonic acid with anhydrous nitric acid.[2] (The latter affords a greatly superior preparative method.) The spectrometer and cells were the same as described previously.[3] In the spectral region between 2 and 16μ there are four strong characteristic bands, at approximately 1700, 1340, 1275, and 795 cm^{-1} respectively. These allow ready detection and quantitative estimation of nitryl chloride in gaseous mixtures.

Immediately after preparation, mixtures of gaseous Cl_2 and N_2O_4 (both at partial pressures of the order of 100 mm Hg) displayed only the bands of N_2O_4 and NO_2. On standing at room temperature there was noted the gradual appearance of the above $ClNO_2$ spectrum accompanied by those characteristic respectively of N_2O_5[3] and $ClNO$. (The latter has two moderately strong bands at approximately 1790 and 920 cm^{-1}.) Concentrations of the various components became practically constant after some ten hours at room temperature. That these final concentrations correspond closely to chemical equilibrium was shown by variation of the initial concentration of Cl_2 and N_2O_4.

It is apparent that equilibrium in the reaction

$$Cl_2 + N_2O_4 \rightleftharpoons 2ClNO_2$$
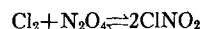
is rather slowly attained, but that it corresponds to a much greater stability of $ClNO_2$ than had previously been supposed. Variation of temperature over a considerable range indicated that the formation of $ClNO_2$ by the above reaction is an *exothermic* process. The reaction

$$N_2O_5 + ClNO \rightarrow N_2O_4 + ClNO_2$$
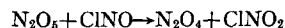
had previously been studied, using a different method, by Mr. Ralph Weston at Stanford University (these studies will be reported elsewhere), and found to be extremely rapid. It is apparent that this equilibrium is also established in the present system, with comparable concentrations of $ClNO$ and $ClNO_2$.

It was further found that the spectrum of $ClNO_2$ appeared in mixtures of O_2 and $ClNO$, the rate increasing rapidly with addition of N_2O_4. The equilibrium

$$2ClNO + O_2 \rightleftharpoons 2ClNO_2$$