``Glass Electrode Behavior in Acid Solutions"

Malcolm Dole

Letters to the Editor

THIS section will accept reports of new work, provided these are terse and contain few figures, and especially few half-tone 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 ($8.00 per page) will not be made and no reprints will be furnished free.

The Infra-Red Spectrum of Nitrosyl Chloride

JOHN H. WISE AND JACK T. ELMER
Department of Chemistry, Stanford University, Stanford, California
July 31, 1950

THE effect of nitrosyl chloride as a possible contaminant due to reaction between various nitrogen compounds and the rock salt windows on infra-red gas cells has led to a re-examination of the infra-red spectrum of nitrosyl chloride. Bailey and Cassie[1] have reported the spectrum, but serious doubt of their assignment of fundamental frequencies was raised by the results of Beeson and Yost.[2] The latter authors proposed a different assignment based on the electron diffraction data of Ketelaar and Palmer[3] and some calculations involving Lechner's formulas.[4]

In the present research, nitrosyl chloride was prepared in two ways: by passing N_2O_4 over a column of damp KCl, and by a direct combination of Cl_2 with NO. The first procedure produced an impure, condensable, mixture consisting of N_2O_4, ClNO, and $ClNO_2$. This observation confirms the results of Ogg and Wilson[5] on the oxidation of ClNO by O_2 since oxygen was not rigidly excluded during the preparation. In the second procedure, tank chlorine was purified by the method described by Beeson and Yost,[2] and the nitric oxide was generated by a similar procedure to that of Johnston and Giauque.[6] The gases were collected in graduated traps, and then evaporated into the evacuated system. The mixture of gases, containing an excess of NO, was frozen out with liquid air and allowed to stand for about 36 hours in a bath originally containing dry ice and acetone. After refreezing in liquid air, the excess NO was removed by pumping from a dry ice bath. Unfortunately, a trace of N_2O_4 was detected in the product. The spectra were taken on a Perkin-Elmer Model 12-C Spectrometer using a 10-cm glass cell with NaCl or KBr windows.

The observed spectrum of nitrosyl chloride differs somewhat from that reported by Bailey and Cassie,[1] particularly their band at 633 cm⁻¹. A comparison of the various assignments is given in Table I. The assignment offered as a result of this work is similar to Beeson and Yost's[2] proposal of the most reasonable choice based on Bailey and Cassie's[1] results. Definite indication of absorption in the 650 cm⁻¹ region is found, but the position was not accur-

TABLE I. Vibrational frequencies of ClNO.

Bailey and Cassie			Beeson and Yost proposals		This research				
ν (cm⁻¹)	Inten.	Assign.	ν (cm⁻¹)	Assign.	ν (cm⁻¹)	Assign.	ν (cm⁻¹)	Inten.	Assign.
					317	ν_2			
			290	ν_2	462	ν_3			
633	6	ν_2	633	ν_3	633	$2\nu_2$	594	VS	ν_3
							670	W?	$2\nu_2$
923	10	ν_3	923	$\nu_2+\nu_3$	923	$2\nu_3$	921	S	$\nu_2+\nu_3$
1200	3	$2\nu_2$					1185	W	$2\nu_2$
									or
									$\nu_1-\nu_3$
1832	7	ν_1	1832	ν_1	1832	ν_1	1800	VS	ν_1
2155	4	$2\nu_2+\nu_3$					2130	S	$\nu_1+\nu_2$
							2390	M	$\nu_1+\nu_3$
							3562	S	$2\nu_1$
							>4000	M	?

ately determined. The calculated value of the entropy of ClNO using Beeson and Yost's[2] Eq. (16) and substituting 327, 594, and 1800 cm⁻¹ for the fundamentals gives:

$$S°_{ClNO} = 4R\ln T + S_{327} + S_{594} + S_{1800} + 15.460 \text{ E.U.}$$
$$= 62.466 \text{ E.U. at } 298°K.$$

This compares favorably with the value 63.0 ± 0.3 cal./deg. found from thermal data.

[1] Bailey and Cassie, Proc. Roy. Soc. (London) A145, 336 (1934).
[2] Beeson and Yost, J. Chem. Phys. 7, 44 (1939).
[3] Ketelaar and Palmer, J. Am. Chem. Soc. 59, 2629 (1937).
[4] Lechner, Monatshefte für Chem. 61, 385 (1932).
[5] Ogg and Wilson, J. Chem. Phys. 18, 900 (1950).
[6] Johnston and Giauque, J. Am. Chem. Soc. 51, 3194 (1933).

"Glass Electrode Behavior in Acid Solutions"

MALCOLM DOLE
Department of Chemistry, Northwestern University, Evanston, Illinois
July 31, 1950

UNDER the above title, Sinclair and Martell[1] have replied to my criticism[2] of their earlier paper[3] in which these authors advocated a negative ion theory for the acid solution errors of the glass electrode. In this most recent note Sinclair and Martell object to my description of the attack of hydrogen fluoride on glass as having no bearing on the interpretation of the results of their work in which they used sulfuric and hydrochloric acids. In my letter, I quoted our former work with hydrogen fluoride as a spectacular example of the way in which chemical attack on the glass surface can destroy the reversible glass electrode e.m.f.'s. I did not, of course, state or imply that the action of hydrofluoric acid is chemically similar to that of sulfuric or hydrochloric acid. I shall now explain in detail what is believed to be the action of strong acids such as sulfuric and hydrochloric on glass surfaces. In this connection I would like to refer to the excellent new book of Kratz,[4] in which his extensive work[5] on the chemical properties of glass surfaces is summarized. When Corning 015 glass electrodes are immersed in water, alkali is leached out of the surface leaving a layer or "skin" of hydrated silicic acid gel as residue. In contact with strong acids in which the vapor pressure of water has been significantly lowered, the surface film of silicic acid is dehydrated, the asymmetry potential is increased, the rate at which the glass gives up alkali to pure water is increased, the electrical resistance of the glass membrane is increased, and the hydrogen electrode function of the glass surface impaired. This is what I meant in my note by chemical attack, and its effects on the reversibility of glass electrode e.m.f.'s. I hope that this explanation of the mechanism of chemical attack clarifies my criticism of the negative ion theory of Sinclair and Martell.

[1] E. E. Sinclair and A. E. Martell, J. Chem. Phys. 18, 992 (1950).
[2] M. Dole, J. Chem. Phys. 18, 573 (1950).
[3] E. E. Sinclair and A. E. Martell, J. Chem. Phys. 18, 224 (1950).
[4] L. Kratz, "Die Glaselektrode und ihre Anwendungen" *Wissenschaftliche Forschungsberichte*, Vol. 59 Frankfurt, 1950.
[5] L. Kratz, *Glastechn. Ber.* 20, 15, 305 (1942).

Normal Modes of Ethane

T. S. G. KRISHNAMURTY AND S. SATYANARAYANARAO
Andhra University, Waltair, India
August 9, 1950

THE theory of groups has been successfully used to obtain the normal modes and frequencies of molecules, and the selection rules for spectral lines in the Raman effect and infra-red absorption. In these applications, only symmetry operations of the type rotations, reflections and rotation-reflections are usually

TABLE I.

	E	2C₃	3C₂	3σₕ	4T	9σ_d	2TC₃	6S₂	6TC₂	nᵢ	nᵢ'	Raman	Infra-red
A₁	1	1	1	1	1	1	1	1	1	3	3	P	P
A₂	1	1	1	-1	1	-1	1	-1	1	1	1	f	f
A₃	1	1	-1	1	1	-1	1	1	-1	1	0	f	f
A₄	1	1	-1	-1	1	1	1	-1	-1	3	2	f	P
E₁	2	2	2	0	-1	0	-1	0	-1	0	0	f	f
E₂	2	2	-2	0	-1	0	-1	0	1	0	0	f	f
E₃	2	-1	0	-2	-1	0	2	1	0	0	0	f	f
E₄	2	-1	0	2	-1	0	2	-1	0	0	0	f	f
G	4	-2	0	0	1	0	-2	0	0	4	3	P	P
	24	0	0	0	48	36	0	0	0				
	18	0	6	0	36	36	0	0	12				
	12	0	12	12	24	36	0	24	24				
	6	0	0	0	12	18	0	0	0				

taken into account. However, in some molecules, it may be possible to consider other elements of symmetry, as for example, a twist through 120° of one of the CH_3 groups against the other in the molecule C_2H_6. Using the point group D_{3h}' Howard† obtained the normal modes, etc., of this molecule. In this paper, assuming that the potential energy has the symmetry of the molecule including the twist also, the symmetry characters of the modes and the selection rules for their appearance in the Raman effect and the infra-red absorption are given. The results are tabulated in Table I. Details regarding the normal frequencies will be published separately.

† J. B. Howard, J. Chem. Phys. 5, 442 (1937).

The Vibrational Energy of H₂S*

HARRY C. ALLEN, JR. AND PAUL C. CROSS
Department of Chemistry and Chemical Engineering,
University of Washington, Seattle, Washington

AND

GILBERT W. KING
Arthur D. Little, Inc., Cambridge, Massachusetts
August 1, 1950

THE approximate location of four new band centers in the infra-red spectrum of hydrogen sulfide has enabled the evaluation of the complete quadratic expression for the unperturbed vibrational energies as

$$(E-E_0)\ cm^{-1} = 2651n_\sigma + 2635n_\pi + 1189n_\delta - 26n_\sigma^2$$
$$- 24n_\pi^2 - 6n_\delta^2 - 90n_\sigma n_\pi - 19n_\sigma n_\delta - 20n_\pi n_\delta. \quad (1)$$

Equation (1) yields the unperturbed levels shown in column two of Table I. From the observed perpendicular type bands[1,2] at 9911 cm^{-1} and 10194 cm^{-1}, the Darling-Dennison[3] parameter γ may be evaluated as 47 cm^{-1}. The calculated energy values for the two pairs of interacting levels are listed in column 3 of the table.

The constants in (1) and the Darling-Dennison interaction parameter were evaluated from the unstarred levels in Table I.

TABLE I.

n_σ	n_π	n_δ	Unperturbed	DD resonance
0	0	1	1183[7]	
0	0	2	2354[7]	
0	1	0	2611[4]	
1	0	0	2625[5]	
1	0	1	3789[7]	
1	1	0	5146[7]	
0	2	0	5174 ⎫	*5138[7]
2	0	0	5198 ⎭	*5234[8]
1	1	1	6290[6]	
2	2	0	*10012[8]	
1	3	0	10044 ⎫	9911[1]
3	1	0	10060 ⎭	10194[2]
0	4	0	*10156[8]	
4	0	0	10188[2]	

The absorption in the region[9] of 5146 cm^{-1} shows an overlapping spectrum centered at approximately 5143 cm^{-1} as compared to the calculated value 5138 cm^{-1} for the perturbed (020) band. The appearance of this parallel type band is presumably due to the borrowing of intensity through rotational interaction from the neighboring (110) perpendicular type band just as has been previously indicated in the appearance of the (400) band[2] at 10188 cm^{-1}.

The analysis of the 8μ-region reveals that recent investigators have not detected the P branch.[10-12] The early investigation of Mischke,[13] however, shows a weak P branch extending from 1180 cm^{-1} to nearly 1000 cm^{-1}.

As would reasonably be expected the results described by (1) are analogous to a similar treatment of the water vapor system.[3] The most conspicuous feature of this analysis is the low frequency of the bending fundamental, from 50 to 100 cm^{-1} less than it has recently been considered to be.[14]

[1] P. C. Cross, Phys. Rev. 47, 7 (1935).
[2] Grady, Cross, and King, Phys. Rev. 75, 1450 (1949).
[3] B. T. Darling and D. M. Dennison, Phys. Rev. 57, 128 (1940).
[4] G. M. Murphy and J. E. Vance, J. Chem. Phys. 6, 426 (1938).
[5] R. M. Hainer and G. W. King, J. Chem. Phys. 15, 89 (1947).
[6] Allen, Cross, and Wilson, J. Chem. Phys. 18, 691 (1950).
[7] To be reported shortly.
[8] Not yet observed.
[9] Unpublished data of M. K. Wilson.
[10] A. D. Sprague and H. H. Nielsen, J. Chem. Phys. 5, 85 (1937).
[11] R. H. Noble, Thesis, Ohio State University (1946).
[12] E. A. Wilson, Thesis, Brown University (1947).
[13] W. Mischke, Zeits. f. Physik 67, 106 (1931).
[14] G. Herzberg, Infrared and Raman Spectra of Polyatomic Molecules (D. Van Nostrand Company, Inc., New York, 1945), p. 283.

The Quantum-Mechanical Equation of State

ROBERT W. ZWANZIG
Gates and Crellin Laboratories of Chemistry,*
California Institute of Technology, Pasadena, California
July 18, 1950

IN the last few years there has been some disagreement about the equivalence of the thermodynamic and kinetic pressure of a quantum liquid, with special emphasis on liquid helium II. The kinetic pressure is obtained from the quantum-mechanical virial theorem. Equations of state which do not appear to be identical have been derived from statistical thermodynamics by H. S. Green[1] and J. de Boer.[2] In this note, a simple derivation will be given, which may expose more clearly the assumptions required.

By differentiating the partition function with respect to volume, we get

$$-p = \frac{\partial A}{\partial v} = \sum_j e^{\beta(A-E_j)} \frac{\partial E_j}{\partial v} \quad (1)$$

where all symbols have their usual significance. The dependence of the energy levels of the system on its volume is needed. To get this, we introduce a scale factor, depending on the volume, into the Schrödinger equation for the system, and determine the dependence of the energy levels on this scale factor. This device is related to the one used by H. S. Green to get the classical equation of state, and by de Boer for the quantum-mechanical case. The Hamiltonian operator for the system is

$$H = -\frac{\hbar^2}{2m} \sum_{k=1}^{N} \nabla_{rk}^2 + V(\mathbf{r}_{1s} \cdots \mathbf{r}_N). \quad (2)$$

The potential is assumed to become infinite at the walls. This wall potential is taken into account by requiring eigenfunctions to vanish at the walls. We define a new coordinate system,

$$\mathbf{r}_k = v^{\frac{1}{3}} \mathbf{R}_k \quad (3)$$

where v is the volume of the system. A variation in v corresponds to an expansion or contraction of the system, without any change in its relative shape or configuration. The equation of state that will result will be valid only for such changes in volume. However, when the dimensions of the system are large compared with the