Thus we may conclude that the major anomalies in the melting points and boiling points of the alkali halides result from the influence of the relative sizes of cation and anion, and that deformation phenomena play only a minor role.

Further Radius Ratio Effects

The action of the radius ratio in influencing the axial ratio of tetragonal crystals with the rutile and anatase structures has been evaluated, and shown to agree well with the results of observation.[2] The radius ratio is also of significance for the relative stability of alternative crystal structures, for the variation of interionic distance accompanying transition from one structure to another,[2] for hydrate and ammoniate formation and for the solubility of salts; in short, for all properties dependent on the crystal energy. The potential expressions of this paper are now being applied to the problems of ion formation, valence and the structure of ionic complexes.

Summary

With the aid of an expression for the mutual energy of ions in terms of standard ionic radii it is shown that the ratio of cation radius to anion radius influences the properties of ionic substances. Irregularities in interionic distances, melting points and boiling points of the alkali halides are explained as resulting from this effect.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE MARTIN MALONEY CHEMICAL LABORATORY OF THE CATHOLIC UNIVERSITY OF AMERICA]

ADSORPTION OF SULFUR DIOXIDE BY TITANIA GEL

BY SIMON KLOSKY AND A. J. BURGGRAFF[1]

RECEIVED JANUARY 9, 1928 PUBLISHED APRIL 5, 1928

The object of this investigation was to determine whether a porous body similar to silica gel, but with a more specific attraction for sulfur dioxide, would adsorb it according to Patrick's condensation formula.

Material

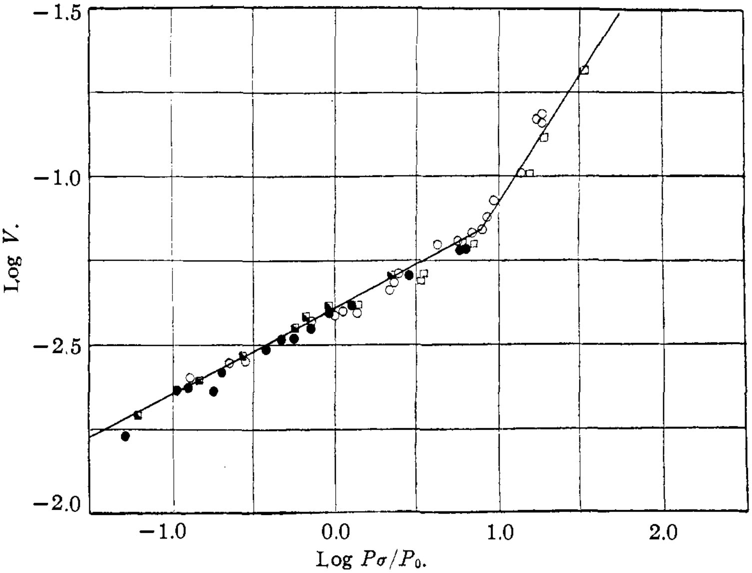
The titania gel was prepared in quantity according to the method of Klosky and Marzano.[2] The sulfur dioxide was taken from the metal tanks which are sold in industry. Its purity was tested by absorbing a known volume in concentrated sodium hydroxide. The gas was completely adsorbed by the sodium hydroxide.

[1] Extract from Doctor's Dissertation, 1927.

[2] Klosky and Marzano, *J. Phys. Chem.*, **29**, 1125 (1925).

The Apparatus

The apparatus used was similar to that used by Patrick and Opdycke.[3] It consisted of flowmeters, which registered any fluctuation in the flow of air or sulfur dioxide above 0.01 cc. per second; a constant temperature bath in which were placed a large cooling coil, a U-tube containing the gel and a sample bottle for the analysis of effluent gases.



◪, 50°; ●, 25°; ○, 0°; □, −22.5°.

Fig. 1.

Manipulation

A mixture of sulfur dioxide and air of constant composition was passed over the gel until no further increase in weight was noticed. The effluent gases were passed through the sample bottle during the entire run. When equilibrium was reached, the U-tube was closed by means of stopcocks and weighed. The sulfur dioxide in the sample bottle was absorbed in a standard iodine solution and the excess iodine titrated with sodium thiosulfate. Knowing the volume of the sample bottle, the external pressure, the temperature of the mixture of gases and the amount of standard iodine solution required, the partial pressure of the sulfur dioxide could be calculated easily. The following table gives the results obtained for four isotherms, where x/m is the weight of sulfur dioxide adsorbed in grams per gram of gel and P is the partial pressure of the sulfur dioxide in millimeters.

---

[3] Patrick and Opdycke, *J. Phys. Chem.*, **29**, 601 (1925).

Table I

Experimental Results

−22.50 °C.		0 °C.		25 °C.	
x/m (g./g.)	p (mm.)	x/m (g./g.)	p (mm.)	x/m (g./g.)	p (mm.)
0.0621	17.35	0.0363	5.50	0.0236	6.60
.0680	17.33	.0400	9.50	.0320	13.20
.0745	42.50	.0405	12.10	.0326	15.70
.0762	43.20	.0535	28.62	.0310	23.60
.9440	78.60	.0565	40.80	.0368	25.98
.0973	93.60	.0584	46.40	.0420	47.50
.1580	185.0	.0690	98.00	.0447	58.00
.2000	253.0	.0736	102.5	.0450	68.00
.3160	440.0	.0824	179.0	.0480	74.00
		.0912	224.1	.0496	95.05
50 °C.		.0973	298.0	.0535	119.0
		.0980	338.6	.0575	158.7
.0226	9.80	.1095	344.0	.0558	164.0
.0266	21.40	.1120	374.0	.0655	271.5
.0326	48.40	.1568	592.0	.0700	362.5
.0385	93.50	.2200	720.0	.0845	758.0
.0470	190.4	.2220	760.0	.0840	760.0
.0500	238.0	.2100	745.0		
.0550	319.8				
.0670	760.0				

Desorption

Several experiments were made on desorption, which was found not to be entirely reversible. A certain amount of sulfur dioxide was found to remain in the gel in every case even after outgassing for several hours.

Calculations

From the weight taken up per gram of gel and the density[4] of sulfur dioxide the volume of liquid sulfur dioxide adsorbed was calculated. From the partial pressure of the sulfur dioxide for the various temperatures and the vapor pressure of liquid sulfur dioxide for the same temperature,[5] the corresponding pressures were calculated. Using values for the surface tension of liquid sulfur dioxide obtained by interpolation of Patrick[6] and Landolt and Börnstein,[7] the term $P\sigma/P_0$ was evaluated, which is used in Patrick's equations.[6] Curve I shows the results when log v is plotted against log $P\sigma/P_0$.

The adsorption affinity, E,[8] was calculated also and plotted against the volume adsorbed. Table II gives in Col. 1 the volume of sulfur

---

[4] Landolt-Börnstein, "Chemical Tables," Vol. I, 285 (1923).

[5] Landolt-Börnstein, "Chemical Tables," Vol. II, 1349 (1923).

[6] McGavack and Patrick, This Journal, **42,** 946 (1920).

[7] Landolt-Börnstein, "Chemical Tables," Vol. I, 242 (1923).

[8] Polanyi, *Verhandl. deut. Physik. Ges.*, **18,** 55 (1916); Berenyi, *Z. physik. Chem.*, **94,** 62 (1920).

dioxide adsorbed by the gel, in Col. 2 the volume read from the curve representing the Polanyi Equation and in Col. 3 the percentage deviation of the former from the latter.

TABLE II

AGREEMENT OF OBSERVED VOLUMES ADSORBED WITH THOSE OBTAINED FROM POLANYI EQUATION

Vol. obs.	Vol. read from curve	Deviation, %	Vol. obs.	Vol. read from curve	Deviation, %
	−22.5° C.			25° C.	
0.0417	0.0426	2.11	0.0350	0.0350	..
.0507	.0502	0.99	.0363	.0370	2.16
.0625	.0620	0.80	.0390	.0382	2.09
.0640	.0670	4.47	.0420	.0410	2.38
.1055	.1035	1.93	.0476	.0460	3.48
.2110	.2110	..	.0510	.0500	2.00
			.0616	.0630	2.22
	50° C.			0° C.	
0.0197	0.0180	9.43	0.0372	0.0370	0.54
.0250	.0240	4.16	.0394	.0395	0.25
.0296	.0292	1.37	.0407	.0410	0.73
.0362	.0340	6.47	.0480	.0480	..
.0386	.0360	7.22	.0687	.0680	1.03
			.1200	.1175	2.13
			.1690	.1690	..

Discussion of Results

When the log of the weight of sulfur dioxide adsorbed per g. of gel is plotted against the log of the partial pressure of sulfur dioxide, the well known Freundlich isotherms are obtained.[9]

Our data show breaks in the isotherms corresponding to the theoretical curve of Coolidge.[10]

The breaks occur on the 0 and −22.5° curves, and at the same volume, as shown by the curve representing the Patrick formula. This is in accord with Patrick's views; however, the breaks occur at a relative pressure of 0.284—contrary to Patrick's Theory, which demands breaks at relative pressures of nearly 1.0. Nevertheless, the Patrick formula is an improvement over that of Freundlich, as it brings all the isotherms on one curve and holds over the same range as the Freundlich equation.

The curve obtained from our data is of the usual shape for the Polanyi Equation.[11]

It represents the data fairly well even in the region beyond the break in the Freundlich curves, with an accuracy that is comparable to that over the region before this.

[9] Freundlich, English Edition of "Capillary Chemistry," **1922**, p. 115.

[10] Coolidge, THIS JOURNAL, **48**, 1798 (1926).

[11] Ref. 9, **1926**, p. 123.

Summary

Adsorption of sulfur dioxide by titania gel has been measured at −22.5, 0, 25 and 50°.

The data have been tested by the equations of Patrick and Polanyi and while the data substantiate Patrick's formula at lower relative pressure, over the whole range they can be best represented by the formula of Polanyi.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY AND FROM THE CRUFT LABORATORY OF HARVARD UNIVERSITY]

THE MEASUREMENT OF THE CONDUCTANCE OF ELECTROLYTES. I. AN EXPERIMENTAL AND THEORETICAL STUDY OF PRINCIPLES OF DESIGN OF THE WHEATSTONE BRIDGE FOR USE WITH ALTERNATING CURRENTS AND AN IMPROVED FORM OF DIRECT READING ALTERNATING CURRENT BRIDGE

BY GRINNELL JONES AND ROSWELL COLT JOSEPHS

RECEIVED JANUARY 9, 1928 PUBLISHED APRIL 5, 1928

Introduction

It would be a pleasure to write an historical review of the previous work on the conductance of electrolytes with appreciative comments on the contributions of many earlier investigators including especially Kohlrausch, Wien, Noyes, Taylor and Acree, Grover and Curtis, Washburn, Kraus, Parker, Miller, Hall and Adams, Morgan and Lammert and many others, but the limitations of space firmly imposed by an Editor who must constantly remember his budget forbid. Moreover, such a review is unessential since the recent paper of Morgan and Lammert[1] contains an excellent summary of the earlier work.

Washburn[2] made substantial improvements in the design of the bridge

---

[1] (a) J. Livingston R. Morgan and Olive M. Lammert, THIS JOURNAL, **48**, 1220 (1926). In addition to the numerous papers referred to in this article the following will be of interest to students of this subject: (b) Wien, *Wied. Ann.*, **58**, 37 (1896); (c) Miller, *Phys. Rev.*, [2] **22**, 622 (1923); (d) Reichinstein, *Z. Elektrochem.*, **15**, 734, 913 (1909); (e) **16**, 916 (1910); (f) **17**, 85, 699 (1911); (g) **19**, 384, 518 (1913); (h) Hall and Adams, THIS JOURNAL, **41**, 1515 (1919); (i) Randall and Scott, *ibid.*, **49**, 636 (1927).

[2] (a) Washburn, THIS JOURNAL, **38**, 2431 (1916); (b) Washburn and Bell, *ibid.*, **35**, 177 (1913); (c) Washburn and Karr Parker, *ibid.*, **39**, 235 (1917). The senior author of this paper was a colleague of Professor Washburn at the University of Illinois while Washburn was engaged in the earlier part of his researches in this field and thus, although not sharing in these investigations directly, had the opportunity of following their progress in detail and acquired at first hand an appreciation of Washburn's important contributions to the measurement and interpretation of conductance of electrolytes. The researches to be described in this and subsequent papers were begun after