

hand, in mixtures containing carbon dioxide the observed values are not only greater than the calculated, but in many cases even exceed the adsorptions found in the absence of the second gas. Pending the accumulation of further data, it is suggested that this anomaly may be due to some kind of mutual interaction between the two kinds of adsorbed molecules.

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NUCLEAR SPIN AND THE THIRD LAW OF THERMODYNAMICS. THE ENTROPY OF IODINE

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RECEIVED NOVEMBER 29, 1930

PUBLISHED FEBRUARY 9, 1931

Much interest is attached to the problem of determining the manner in which nuclear spin is concerned in the application of the third law of thermodynamics. The somewhat complicated but well-established situation which exists in hydrogen has recently been discussed.¹ In this case nuclear spin results in ortho and para forms which establish equilibrium with each other so slowly that it is impractical to use heat capacity measurements to obtain the entropy. However, it was suggested that hydrogen might be the only substance in which nuclear spin would appreciably affect the calorimetric properties at temperatures above a few degrees absolute. If this proves to be true, it will be convenient to ignore the effect of nuclear spin on the absolute entropy except for hydrogen. This would be possible since, as first pointed out by Gibson and Heitler,² for certain gas reactions, the limiting contribution which nuclear spin makes to the entropy cancels in obtaining the entropy change which occurs during a reaction.

The diatomic elements offer a suitable opportunity for obtaining information concerning the above problem and of these the ones consisting primarily of one isotope present the most favorable cases. Diatomic gas molecules which consist of two isotopes of the same element do not have the division of such molecules into ortho and para states. This is the situation most open to suspicion in connection with the possibility of anomalous calorimetric effects. For example, in chlorine the 35-37 molecules would be expected to establish their limiting spin entropy below the lowest attained temperature. The 35-35 and 37-37 molecules are of the type in which we are more interested. Since these latter two would behave differently if the nuclear spins of the two isotopes are different, we believe it best to confine the initial investigation to simpler substances. Of these nitrogen is at present under experimental investigation and existing data on iodine are sufficient for our purpose. In this paper we shall consider the case of iodine.

¹ Giauque, *THIS JOURNAL*, **52**, 4816 (1930).

² Gibson and Heitler, *Z. Physik*, **49**, 465 (1928).

The nuclear spin of iodine is undetermined but it is known to be large. This is determined from the fact that alternation of intensity in the lines of its band spectrum has not been observed.³ This is the limiting case approached when the nuclear spin is large. Elements with spins of a few units give an easily observed intensity alternation. However, it can be shown that the limiting nuclear spin entropy has been essentially established at a temperature of 10°K. and presumably much lower even though we are unaware of its exact value.

The available data consist of heat capacity measurements of several observers on solid iodine extending to below 10°K., various vapor pressure determinations and measurements of the band spectrum of diatomic iodine gas.

The Heat Capacity and Entropy of Iodine.—Of the numerous low temperature determinations of the heat capacity of iodine,⁴ only the series due to Lange can be given any weight as an accurate piece of work. Lange covered only the range from 9 to 52°K. but fortunately even at 52°K. the heat capacity is rapidly approaching the equipartition value. In extending the curve to room temperature a decision had to be made between data with extreme deviations of as much as 6%. In making this decision the value of $C_p - C_v$, which is known from the following thermodynamic relationship, was of considerable importance.⁵

$$C_p - C_v = \frac{\alpha^2 VT}{\beta}$$

where α and β are the coefficients of expansion and compressibility, respectively. Lewis and Gibson⁶ have given the above difference as 0.9 calories/degree per gram atom of iodine at 298.1°K. A repetition of their calculation, using the data given in the "International Critical Tables," raises this somewhat. The value adopted was 1.0 calorie/degree per gram atom at room temperature. When this amount was considered it became evident that the only reasonable C_v curve which could be extended to 298.1°K. passed quite well through the results of Nernst, Koref and Lindemann.^{4a}

On calculating the entropy from the above curve a value was obtained which agreed so closely with that given in the "International Critical Tables" by Rodebush and Rodebush⁷ that the "International Critical Tables" value was adopted except with regard to the estimate of accuracy.

³ For example, see the discussion by Mulliken, *Trans. Faraday Soc.*, **25**, 634 (1929).

⁴ (a) Nernst, Koref and Lindemann, *Berlin Sitzber.*, 247 (1910); (b) Nernst, *ibid.*, 262 (1910); (c) Nernst, *Ann. Physik.*, [4] **36**, 395 (1911); (d) Gunther, *ibid.*, [4] **51**, 828 (1916); (e) Lange, *Z. physik. Chem.*, **110**, 343 (1924).

⁵ Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 136.

⁶ Lewis and Gibson, *THIS JOURNAL*, **39**, 2554 (1917).

⁷ Rodebush and Rodebush, "International Critical Tables," Vol. V, p. 88.

We believe that the value of $S_{298.1^\circ\text{K.}} = 27.9$ calorie/degree per mole of solid iodine (I_2) is reliable to 0.1 unit. This value, as will be shown, is not the absolute entropy of iodine, but is, as we shall now assume, the absolute entropy less the unknown amount of the limiting nuclear spin entropy.

The entropy of gaseous iodine may be obtained from the band spectrum for this substance. A summary of the spectroscopic data with references has been given by Birge.⁸

$$S^\circ = \frac{3}{2}R \ln M + \frac{5}{2}R \ln T - R \ln P + \frac{5}{2}R - 7.267 + R \ln Q + RT \frac{d \ln Q}{dT}$$

where $Q = \sum p e^{-\epsilon/kT}$, p is the *a priori* probability and ϵ the energy of the state concerned. The other symbols in the above expression have their usual significance. In evaluating Q the vibrational energies were obtained from the expression

$$\epsilon_v \text{ (in cm.}^{-1}\text{)} = 214.26 (v + \frac{1}{2}) - 0.592 (v + \frac{1}{2})^2$$

where $v = 0, 1, 2, 3$, etc. This formula yields the same values as the older type given in "Molecular Spectra in Gases,"⁸ but has been converted to the later nomenclature which recognizes the existence of one-half unit of zero point vibration.

In considering the rotation the approximation $Q_r = 4\pi^2 I kT/h^2$ was sufficiently accurate for our present purpose since the rotational deformation of the iodine molecule is not great. This value of Q_r takes into consideration the fact that the symmetry of the iodine molecule reduces the number of states, and thus Q_r , by a factor of two.

$$I = 742.6 \times 10^{-40} \text{ g. cm.}^2 = \text{the moment of inertia}$$

$$Q = Q_v Q_r = \frac{4\pi^2 I kT}{h^2} \sum_{v=0}^{\infty} e^{-h c \epsilon_v / kT}$$

The values used for all natural constants are those given in the "International Critical Tables." The rotational approximation leads to

$$RT \frac{d \ln Q_r}{dT} = R = 1.9869 \text{ calories/degree per mole}$$

$$\begin{aligned} RT \frac{d \ln Q}{dT} &= R \left[T \frac{d \ln Q_r}{dT} + T \frac{d \ln Q_v}{dT} \right] \\ &= R \left[1 + \frac{hc}{kT} \frac{\sum \epsilon_v e^{-h c \epsilon_v / kT}}{\sum e^{-h c \epsilon_v / kT}} \right] \end{aligned}$$

From the above we find

$$\begin{aligned} S_{298.1}^\circ &= S_{\text{Translation}} + S_{\text{Rotation}} + S_{\text{Vibration}} \\ &= 42.50 + 17.75 + 2.04 \\ &= 62.29 \text{ calories/degree per mole} \end{aligned}$$

The value 62.29 E. U. is the absolute entropy of iodine less the amount due to nuclear spin.

⁸ Birge, "Molecular Spectra in Gases," Bull. Nat. Res. Council, Vol. 11, Part 3, p. 231.

⁹ Giauque, THIS JOURNAL, 52, 4808 (1930).

The ΔS for the vaporization of iodine could be calculated from the above data and compared with that found from the vapor pressure data. However, a more severe test of the individual experimental data will be made.

The Heat of Vaporization of Iodine

$$\begin{aligned} F^\circ &= H^\circ - TS^\circ \\ &= E_0^\circ + RT^2 \frac{d \ln Q_v}{dT} + \frac{7}{2} RT - TS^\circ \end{aligned}$$

where E_0° is the energy content of perfect molecular iodine gas at the absolute zero. From the data given above

$$\begin{aligned} F_{298.1}^\circ &= E_0^\circ + 342 + 3.5 \times 1.9869 \times 298.1 - 298.1 \times 62.29 \\ &= E_0^\circ - 16,154 \text{ calories for } I_2 \text{ gas} \\ H_{298}^\circ &= E_0^\circ + 2415 \text{ calories} \end{aligned}$$

From Rodebush and Rodebush⁷

$$\begin{aligned} F_{298.1}^\circ &= E_0^\circ - 5137 \text{ calories for } I_2 \text{ solid} \\ H_{298.1}^\circ &= E_0^\circ + 3178 \text{ calories} \end{aligned}$$

Therefore $\Delta F_{298.1}^\circ = \Delta E_0^\circ - 11,017$. With sufficient accuracy the value of $C_{p(g)} - C_{p(s)}$ may be taken as $9.0 - 13.0 = -4.0$ calories/degree per mole between 0 and 100°. Then for the above range $\Delta H_T = \Delta E_0^\circ + 429 - 4.0 T$

$$\frac{d(\Delta F/T)}{dT} = - \frac{\Delta H}{T^2}$$

Evaluating the integration constant from the value of $\Delta F_{298.1}^\circ$

$$\begin{aligned} \Delta F^\circ &= \Delta E_0^\circ + 429 + 4.0 T \ln T - 61.186 T \\ &= -RT \ln P \end{aligned}$$

where P is the vapor pressure of iodine in atmospheres. From this equation each measurement of vapor pressure gives a value of ΔE_0° .

The value of ΔE_0° should remain constant if our assumption that the nuclear spin entropy has reached its limiting value below 10°K. is correct.

The results from the data of Baxter, Hickey and Holmes¹⁰ and of Baxter and Grose¹¹ are given in Table I.

In Table II the earlier and somewhat less accurate data of Ramsay and Young¹² are considered for completeness but are given no weight.

Before proceeding with the main object of this paper, we will pause to obtain a very reliable equation for representing the vapor pressure of solid iodine. Taking $\Delta E_0^\circ = 15,640$, we find

$$\begin{aligned} -RT \ln P \text{ (atm.)} &= 16,069 + 4.0 T \ln T - 61.186 T, \text{ or} \\ \log P \text{ (atm.)} &= - \frac{3512.3}{T} - 2.013 \log T + 13.374 \end{aligned}$$

¹⁰ Baxter, Hickey and Holmes, *THIS JOURNAL*, 29, 127 (1907).

¹¹ Baxter and Grose, *ibid.*, 37, 1061 (1915).

¹² Ramsay and Young, *J. Chem. Soc.*, 49, 453 (1886).

TABLE I
HEAT OF SUBLIMATION OF IODINE AT THE ABSOLUTE ZERO

| Temperature, degrees absolute | Vapor pressure, mm. | ΔE_0° calories per mole | Observers |
|----------------------------------|------------------------|---|---------------|
| 273.1 | 0.030 | 15655 | B., H. and H. |
| 288.1 | .031 | 15633 | B., H. and H. |
| 298.1 | .305 | 15630 | B., H. and H. |
| 303.1 | .469 | 15640 | B., H. and H. |
| 308.1 | .699 | 15640 | B., H. and H. |
| 313.1 | 1.025 | 15643 | B., H. and H. |
| 318.1 | 1.498 | 15639 | B., H. and H. |
| 323.1 | 2.154 | 15639 | B., H. and H. |
| 323.1 | 2.154 | 15639 | B. and G. |
| 328.1 | 3.084 | 15633 | B., H. and H. |
| 328.1 | 3.069 | 15636 | B. and G. |
| 333.1 | 4.285 | 15647 | B. and G. |
| 338.1 | 5.962 | 15643 | B. and G. |
| 343.1 | 8.196 | 15640 | B. and G. |
| 348.1 | 11.21 | 15637 | B. and G. |
| 353.1 | 15.09 | 15639 | B. and G. |
| 358.1 | 20.21 | 15639 | B. and G. |
| 363.1 | 26.78 | 15640 | B. and G. |
| 368.1 | 35.24 | 15640 | B. and G. |

Average 15640 = 3 calories (av. dev.)

TABLE II
HEAT OF SUBLIMATION OF IODINE AT THE ABSOLUTE ZERO
Data of Ramsay and Young

| Temperature, degrees absolute | Vapor pressure, mm. | ΔE_0° calories per mole | Temperature, degrees absolute | Vapor pressure, mm. | ΔE_0° calories per mole |
|-------------------------------------|---------------------------|--|-------------------------------------|---------------------------|--|
| 331.2 | 4.9 | 15467 | 364.9 | 28.95 | 15656 |
| 337.6 | 6.05 | 15608 | 365.0 | 29.6 | 15644 |
| 339.4 | 6.25 | 15664 | 369.9 | 37.8 | 15660 |
| 348.3 | 11.5 | 15628 | 375.8 | 50.65 | 15674 |
| 353.5 | 15.15 | 15653 | 378.8 | 59.85 | 15665 |
| 359.1 | 21.25 | 15644 | 386.9 | 87.0 | 15689 |

An accurate value of $\Delta H_{298.1}$ for the sublimation of iodine may be calculated from

$$\Delta H_T = 15,640 + 429 - 4.0 T$$

$$\Delta H_{298.1} = 14,877 \text{ calories per mole}$$

This value is more reliable than the value of ΔE_0° , since any error in the 429 calorie term which appears in the equation does not affect the constancy of the ΔE_0° calculated. However, since the value of ΔE_0° would be shifted by an exactly compensating amount, a reliable value of ΔH is assured. It may be well to add that there is no reason for questioning the reliability of ΔE_0° .

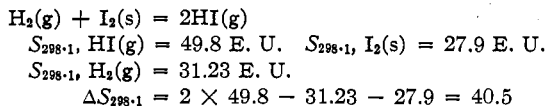
The excellent constancy of ΔE_0° in Table I is a substantial proof of the assumption on which the calculation was based. If, for example, the effect

of nuclear spin appeared in the heat capacity measurements above 10°K. to an extent which caused an effect of one entropy unit, a linear trend of about 100 calories would have been evident in ΔE_0^0 . Thus the data on iodine confirm the idea that the $\int_0^T C_p d \ln T$ with the usual extrapolation below a few degrees absolute will usually ignore the effect due to nuclear spin. As mentioned above, this is not even approximately true in the case of hydrogen, but this substance is unusual in many ways; for example, unlike all other substances it condenses at temperatures far below those at which the limiting high temperature spin distribution is approached. Since Bonhoeffer and Harteck¹³ have shown that the perturbing effects of increased pressure are effective in restoring equilibrium in the case of hydrogen at room temperature, it would be expected that the intimate contact associated with condensation would be even more effective. However, in hydrogen, condensation does not occur until such low temperatures have been reached that the rate has been decreased sufficiently to permit the establishment of a false equilibrium.

In iodine the results indicate that the ortho molecules, which have the rotational quantum numbers $j = 1, 3, 5 \dots$, do not carry the rotational multiplicity of the lowest ortho state, namely, $p = 2j + 1 = 2 \times 1 + 1 = 3$, into the solid as is the case with hydrogen. However, the results indicate that both para and ortho iodine carry their respective spin multiplicities into the solid state.

We have had many interesting discussions of the above results with Professor Linus Pauling, who has recently¹⁴ given a quantum mechanical discussion of the conditions under which molecules may possess rotational quantum levels in the solid state. Pauling has expressed the difference between the hydrogen and iodine cases as follows: the rotational quanta of the hydrogen molecule involve energies and forces which are large compared to the similar quantities concerned in crystalline hydrogen; thus crystallization is unable to prevent rotational motion. In the case of iodine with its relatively very small rotational quanta and relatively large crystal forces, rotation within the solid becomes impossible.

To illustrate the way in which the third law should be used, we will consider the reaction



In no case is the given entropy value the absolute entropy. In the case of hydrogen the value⁹ 31.23 was obtained by reducing the known absolute

¹³ Bonhoeffer and Harteck, *Z. physik. Chem.*, [B] 4, 113 (1929).

¹⁴ Pauling, *Phys. Rev.*, 36, 430 (1930).

entropy by the amount due to the nuclear spin effect. In the case of hydrogen iodide¹⁵ the effect of nuclear spin has not been observed either in the band spectrum or in the low temperature heat capacity measurements and is thus eliminated. For solid iodine we have seen above that the heat capacity with the usual extrapolation at very low temperatures has eliminated the effect of the nuclear spin which it is known to possess. Thus by a simple artifice the cancellation of nuclear spin entropy effect has been accomplished and the correct entropy change during reaction has been obtained.

Were it possible to measure the heat capacity sufficiently close to the absolute zero of temperature, the correct absolute entropy would be obtained but this is not practicable. Thus it appears necessary to make the very plausible assumption that the usual methods of obtaining entropy, while not absolute, for the reasons given above, will lead to correct entropy changes in reactions, except in the case of hydrogen, where the adjusted value given above may be used.

Further investigations are necessary and are being undertaken to find if substances other than hydrogen deviate from the proposed rule.

Summary

The heat capacity, vapor pressure and spectroscopic data on iodine have been used to obtain accurate values for the heat of sublimation and entropy of iodine.

The heat of sublimation of iodine was found to be 15,640 calories per mole at the absolute zero and 14,877 calories per mole at 298.1°K.

With the assistance of the spectroscopic data a reliable equation for the vapor pressure of solid iodine has been obtained.

$$\text{Log}_{10} P \text{ (atm.)} = - \frac{3512.3}{T} - 2.013 \log_{10} T + 13.374$$

$$S_{298.1}, I_2(s) = 27.9 \pm 0.1 \text{ calories/degree per mole}$$

$$S_{298.1}, I_2(g) = 62.29 \text{ calories/degree per mole}$$

These quantities are not the absolute entropies of iodine but are less than the absolute entropies by the amount of entropy due to nuclear spin. This amount is at present unknown.

The values given can be used in combination with other such values to obtain entropy changes accompanying chemical reactions.

It has been determined that the limiting high temperature entropy effect due to nuclear spin in iodine persists to temperatures below 10°K. This is important since if, as expected, this characteristic proves to be general except for the known exception of hydrogen, it will greatly simplify the complications introduced by nuclear spin in connection with the application of the third law of thermodynamics.

¹⁵ Giauque and Wiebe, *THIS JOURNAL*, 51, 1441 (1929).

Although odd and even rotation species exist in diatomic iodine gas, the data show that molecular rotation of the type existing in solid hydrogen does not occur in solid iodine. However, the results indicate that both para and ortho iodine carry their respective spin multiplicities into the solid state.

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[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY OF BROWN UNIVERSITY]

PHOTOCHEMICAL STUDIES.

XII. THE PHOTOCHEMICAL REACTION BETWEEN NITRIC OXIDE AND MERCURY VAPOR

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RECEIVED NOVEMBER 29, 1930

PUBLISHED FEBRUARY 9, 1931

The field of investigation initiated by the fundamental researches of Cario¹ and of Cario and Franck,² in which the spectra of thallium and of silver and the dissociation of hydrogen were produced through the agency of excited mercury atoms, has proved to be of great theoretical interest. These phenomena, ascribed to inelastic collisions of the second kind, have been shown to be quite universal and have been demonstrated for a large variety of reactions by many different workers. It is not necessary at this point to give a detailed list of such reactions.³

The exact mechanism of such photosensitized reactions is of some interest. The various experimental facts and theoretical ideas concerning the action of excited mercury on hydrogen and water vapor have been summarized and discussed recently by Beutler and Rabinowitsch.⁴ The production of ozone from oxygen, first studied by Dickinson and Sherrill,⁵ has been investigated from different angles by other investigators.⁶ Various mechanisms have been proposed to account for this reaction⁷ and among others one which depends, essentially, on the fact that oxygen is paramagnetic. It was with the object of throwing further light upon the mechanisms of some types of photosensitization that the present investigation, involving also the action of excited mercury on a paramagnetic gas, nitric oxide, was undertaken.

¹ Cario, *Z. Physik*, 10, 185 (1922).

² Cario and Franck, *ibid.*, 11, 161 (1922).

³ For a recent summary see Griffith and McKeown, "Photo-processes in Gaseous and Liquid Systems," Longmans, Green and Co., London, 1929, p. 582 *et seq.*

⁴ Beutler and Rabinowitsch, *Z. physik. Chem.*, 8B, 403 (1930).

⁵ Dickinson and Sherrill, *Proc. Nat. Acad. Sci.*, 12, 175 (1926).

⁶ Noyes, *THIS JOURNAL*, 49, 3100 (1927); Leipunsky and Sagulin, *Z. physik. Chem.*, 1B, 362 (1928); 3B, 215 (1929); Noyes, *ibid.*, 2B, 445 (1929).

⁷ See also Gaviola, *Phys. Rev.*, 33, 309 (1929).