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# Mass-Spectrometric Study of the Sublimation of MnS(s) and the Dissociation Energy of MnS(g)

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Mass-spectrometric measurements on stoichiometric MnS and a mixture of MnS and graphite in tungsten crucibles show that the former vaporizes congruently to produce Mn(g) and  $\frac{1}{2}S_2(g)$  and that the latter system reacts to form Mn(g) and CS(g). Small quantities of MnS<sup>+</sup>, MnS<sup>+</sup>, MnS<sup>+</sup>, sulfur polymers, and possibly Mn2<sup>+</sup> and Mn2<sup>+</sup> were also observed. Intensity measurements on Mn<sup>+</sup>, S<sup>+</sup>, S2<sup>+</sup>, and MnS<sup>+</sup> and previously measured decomposition pressures of MnS were combined in a third-law treatment to yield for the dissociation energy of MnS(g) 71±4 kcal/mole. The associated heat of formation from solid elements is  $67\pm 6$  kcal/mole. The thermodynamic results are given in Eqs. (4) to (9). Very approximate values of energies for dissociation of a sulfur atom from MnS2 and MnS3 are given.

N connection with studies of the manganese sulfide-. carbon system by Wiedemeier and Schäfer<sup>1</sup> information about the importance of the vaporization of MnS itself was required. Knudsen effusion measurements were performed on MnS in Mo crucibles by the same authors.<sup>2</sup> They demonstrated that MnS vaporizes congruently, and they assumed that the reaction,

$$MnS(s) = Mn(g) + \frac{1}{2}S_2(g),$$
 (1)

is the predominant one. To reveal the actual mode of vaporization of MnS and, hence, to remove the necessity of this assumption, a mass-spectrometric investigation of the vaporization of MnS has been undertaken. We have also studied mass spectrometrically the reaction,

$$MnS(s) + C(s) = Mn(g) + CS(g), \qquad (2)$$

from which Wiedemeier and Schäfer<sup>1</sup> deduced the heat of formation of CS(g).

The present work shows that Reactions (1) and (2) were indeed the predominant ones in the two cases and that small amounts of S(g) and MnS(g)and minute amounts of other species were also observed in the MnS case. This report gives the dissociation energy of MnS(g) as derived from the absolute partial pressure of Mn(g) obtained from the earlier Knudsen effusion measurements<sup>2</sup> and the mass-spectrometric intensities of S<sup>+</sup> and MnS<sup>+</sup>.

#### EXPERIMENTAL

The instrument used for this investigation was a high-temperature first-order direction-focusing, 12-in.radius, 60° magnetic sector Dempster-type mass spectrometer built by Nuclide Analysis Associates, State College, Pennsylvania.

During the operation periods, the pressure in the crucible region was of the order of 10<sup>-6</sup> mm Hg, and in the source and analyzer regions, of the order of  $10^{-7}$ and 10<sup>-8</sup> mm Hg, respectively.

A moveable slit between the crucible region and the ion-source region was used as a shutter so that the intensity of the ion beam actually arising from neutral species originating in the crucible was measured.

The temperature was read by means of a Leeds & Northrup optical pyrometer which was sighted through a prism and an optical window into the black-body hole in the bottom of the crucible. The pyrometer was calibrated by the National Bureau of Standards. Prism and window corrections were determined in the usual way with a tungsten-filament lamp.

The tungsten Knudsen crucible was 30-mm outside height, 19-mm outside diameter, 18-mm inside height, and 13-mm inside diameter. It was closed with a tightfitting tungsten lid containing a sharp-edged effusion hole in the center. The orifice area was determined microscopically to be  $8.495 \times 10^{-3}$  cm<sup>2</sup>. Before the investigation, the crucible was outgassed in a separate system under high vacuum at 1950°C to constant weight.

The sample was a portion of the same preparation of the stable, green modification of MnS which had been used in the previous work.<sup>2</sup> It had been prepared by precipitation and had been purified by heating small quantities in H<sub>2</sub>S at 450°C for 4 h. A new analysis gave 63.19% Mn and 36.88% S (theoretical values: 63.14% and 36.86%) and differed from the earlier analysis by only 0.01%. Manganese was determined by titration with EDTA, and sulfur was precipitated as BaSO<sub>4</sub>. Chemical analysis and x-ray photographs taken after vaporization of about 50% of the sample showed that the residual sample had the stoichiometric composition.

About 1.5 g of the sample was weighed into the outgassed crucible. The assembly was slowly heated each day to about 1400°C in the mass spectrometer. Mass spectra and ionization-efficiency data were taken

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<sup>&</sup>lt;sup>1</sup>H. Wiedemeier and H. Schäfer, Z. Anorg. Allgem. Chem. **326**, 235 (1963–1964).

<sup>&</sup>lt;sup>2</sup> Reference 1, p. 230.

		Multiplier (V) 70 eV	Faraday cup collector (10 <sup>-5</sup> V)				
Mass	Species		70 eV	45 eV	20 eV	12 eV	
55	Mn	288ª	79.5	76.5	36.0	10.5	
64	S2	204ª	38.2	33.8	12.0	3.0	
32	S	26.7	7.5	6.0	1.5	0.4	
87	MnS	0.96					
96	S <sub>3</sub>	$7.0 \times 10^{-3}$					
110	Mn <sub>2</sub> ?	0.12					
119	$MnS_2$	$7.8 \times 10^{-3}$					
128	S4	2.1×10 <sup>-3</sup>					
151	MnS <sub>3</sub>	9.0×10-4					
165	$Mn_3$ ?	5.0×10-4					

TABLE I. Mass spectrum of species over MnS at 1664°±5°K.

<sup>a</sup> Measurement which was made at 0.12-mA electron current was corrected to 1.2 mA.

over a fortnight. No change in the character of the spectrum was observed during the experiments.

For the investigation of Reaction (2), the crucible was loaded with 1 g of the above described MnS and 0.5 g of spectral carbon powder of highest purity. The proportions correspond to a molar ratio MnS:C=1:4.

## RESULTS

## **Vaporization Reactions**

The results of a systematic mass scan over the entire spectrum up to approximately mass 500 at 1664°±5°K are listed in Table I. Columns 3-7 contain the intensities for the indicated electron energies expressed in volts as obtained from the recorder. No other species except normal background ones was found.

Both the multiplier and the collector results show that Mn(g) and  $S_2(g)$  are the principal species in the vapor and prove the correctness of the assumption made in the previous work<sup>2</sup> that Reaction (1) is the predominant one in the vaporization of MnS. Diatomic MnS(g) constitutes 0.3% or less of the vapor.

## Dissociation Energy of MnS(g)

Ionization-efficiency curves for  $Mn^+$  and  $S_2^+$  had normal shapes, and that for S<sup>+</sup> showed a distinct break at about 15 V owing to the onset of fragmentation of  $S_2$ . The collector intensities in Table I show the increasing degree of fragmentation of S<sub>2</sub> with increasing electron energy.

The dissociation energy was obtained from a thirdlaw treatment of the data. Values for the dissociation equilibrium constant for MnS(g) were obtained in three ways. The collector intensities at 1664°K for Mn<sup>+</sup> and S<sup>+</sup> and the multiplier intensity for MnS<sup>+</sup> for 20-V electrons were used to obtain the intensities of S<sup>+</sup> and MnS<sup>+</sup> relative to that for Mn<sup>+</sup>. The pressures of S(g) and MnS(g) relative to that of Mn(g)

were obtained by using the cross sections of each and the multiplier gain for MnS+. Multiplication of these relative pressures by the pressure of Mn(g) at the same temperature,  $8.53 \times 10^{-6}$  atm, as calculated from the Knudsen effusion vapor-pressure measurements<sup>2</sup> gave the partial pressures from which the equilibrium constant was calculated.

The second method of calculation used the same pressure of MnS(g), but the S(g) pressure was calculated from the Knudsen pressure of  $S_2(g)$ <sup>2</sup> and the dissociation energy of  $S_2(g)$  taken as 101 kcal/mole, which is the presently accepted value.<sup>1,3-6</sup>

The third method used values of intensities for Mn<sup>+</sup>, S<sup>+</sup>, and MnS<sup>+</sup> obtained for 20-V electrons with the multiplier alone in temperature-coefficient measurements. Measurements were made at several different temperatures for each species and were plotted. Values at selected temperatures were taken from the curves for the different species and were converted into pressures in the same way as for the other methods.

The elemental cross sections were taken from Otvos and Stevenson<sup>7</sup> and were added to obtain molecular cross sections. The values used were Mn, 30.1; S, 12.8;  $S_2$ , 25.6; and MnS, 42.9. The multiplier gains for Mn<sup>+</sup> and S<sup>+</sup> as obtained from Columns 3 and 4 in Table I are both  $3.6 \times 10^5$ . The value for S<sub>2</sub><sup>+</sup> is  $5.3 \times 10^5$  which is nearly <sup>3</sup>/<sub>4</sub> that for Mn<sup>+</sup> and S<sup>+</sup>. On the basis of these results it is assumed that the multiplier gain for MnS<sup>+</sup> is the same as for the other diatomic ion,  $S_2^+$ .

That the relative cross sections are correct to within a factor of 2 is revealed by the fact that the relative pressures calculated from the collector intensities and the cross sections are consistent with the previously

<sup>&</sup>lt;sup>3</sup> J. Berkowitz and J. R. Marquart, J. Chem. Phys. 39, 275 (1963). <sup>4</sup>L. Brewer, J. Chem. Phys. **31**, 1143 (1959).

<sup>&</sup>lt;sup>6</sup> D. G. H. Marsden, J. Chem. Phys. **31**, 1144 (1959). <sup>6</sup> R. Colin, P. Goldfinger, and M. Jeunehomme, Nature **187**, 408

<sup>(1960).</sup> <sup>7</sup> J. W. Otvos and D. P. Stevenson, J. Am. Chem. Soc. 78, 546 (1956).

established congruence of the vaporization process within 30% and are consistent with the S<sub>2</sub>-S equilibrium pressures within a factor of 2.

Free-energy functions for Mn(g) and S(g) are tabulated by Stull and Sinke.<sup>8</sup> Values for MnS(g) were calculated from estimated molecular parameters. The internuclear distance was calculated by means of the rule of Schomaker and Stevenson.9 Bond radii of Pauling<sup>10</sup> and electronegativities of Gordy and Thomas<sup>11</sup> gave  $r_e = 2.18$  Å for MnS(g) for this purpose. Badger's rule<sup>12</sup> and the internuclear distance gave the vibrational frequency:  $\omega_e = 661 \text{ cm}^{-1}$  for MnS(g). The electronic degeneracy for MnS was taken to be 2 corresponding to postulated  $^{2}\Sigma$  state.

The results are given in Table II in which the temperatures, intensities, and pressures are given for each species as required for the method of calculation given in the first column. The final column gives the dissociation energies  $\Delta H_0^{\circ}$  as obtained from the two preceding columns which contain the dissociation constant and the change in the free energy functions according to the equation

$$\Delta H_0^{\circ} = T\{-R\ln K - \left[(\Delta F^{\circ} - \Delta H_0^{\circ})/T\right]\}.$$
 (3)

The three different methods are indicated by Roman numerals in the first column; the pressures were calculated as just described. We choose for the dissociation energy of MnS(g) the value  $71\pm4$  kcal/mole or  $3.1 \pm 0.2$  eV.

From this dissociation energy can be calculated two other properties of MnS(g), its heat of formation relative to the solid elements and the heat of sublimation of MnS(s) to form MnS(g). The particular values obtained depend on the choice of auxiliary thermodynamic quantities for the system.

Wiedemeier and Schäfer<sup>2</sup> pointed out a slight discrepancy among related quantities amounting to 3 kcal between their value of 137.2 for the heat of sublimation of MnS and the sum of the calorimetric heat of formation of MnS(s) of  $-49.5^{13}$  kcal/mole, the heat of formation of  $\frac{1}{2}S_2(g)$  of 15.4 kcal,<sup>8</sup> and their sublimation energy of Mn of 69.3 kcal/mole.14 The discrepancy might arise from any of the measurements, except the sulfur sublimation energy, or possibly from errors in the heat capacities. This discrepancy is within our error, and we choose  $67\pm 6$  kcal/mole as the heat of formation of MnS(g) and  $116\pm 6$  as its enthalpy relative to MnS(s).

	$H_0^{\circ}$	le <sup>-1</sup> )	3.9	1.0	0.6 1.4	2.3	+4	
TABLE II. The dissociation energy of MnS(g) obtained from mass spectrometry.	г 	r mo_(k		11	22		sen 71	
	$- \frac{\left(\Delta F^{\circ} - \Delta H_0^{\circ}\right)}{\left(\text{cal deg}^{-1}, \text{mole}^{-1}\right)}$		25.656	25.656	25.505 25.656	25.828	Value cho	
	$rac{K}{(10^{-4}  ext{ atm})}$		3.614	1.929	0.713	4.320	:	
		MnS(g)	$1.98 \times 10^{-8}$	$1.98 \times 10^{-8}$	2.69×10 <sup>-9</sup> 1.54×10 <sup>-9</sup>	9.46×10-8		
	i (atm)	$S_2(g)^d$		$4.27 \times 10^{-6}$				
	Pressures	S(g)	8.37×10 <sup>-7</sup>	4.47×10 <sup>-7</sup> •	8.24×10 <sup>-8</sup> 3.06×10 <sup>-7</sup>	1.23×10-	i	
		$Mn(g)^d$	8.53×10 <sup>-6</sup>	8.53×10-6	2.33×10-6 8.53×10-6	3.33×10-		
	ntensities units (V)	s+	1.5×10⁻⁵					44
	Collector i Arbitrary	$Mn^+$	36.0×10 <sup>-5</sup>	36.0×10-⁵				20-in. shutter wid 210-in. shutter wid
	sities (V)	MnS <sup>+</sup>	0.63	0.63	0.07	1.36		current; 0.( current; 0.1 al.
	dier inten ary units	$\mathbf{x}^{+}_{+}$			0.39	3.46		tron-impact tron-impact S <sub>8</sub> ) = 101 kc
	Multip Arbitr	$Mn^+$			26.7	225		1.2-mA elect 1.2-mA elect 1.2-mA elect ents via $D^0($
	- (X°) T		1664	1664	1587 1664	1754		t electrons; t clectrons; sen experim sen experim
		Method	Ia	IIa	٩III			<sup>a</sup> Twenty-vol <sup>b</sup> Twenty-vol <sup>o</sup> From Knud <sup>d</sup> From Knud

<sup>&</sup>lt;sup>8</sup> D. R. Stull and G. C. Sinke, Advan. Chem. Ser. 18 (1956). <sup>9</sup> V. Schomaker and D. P. Stevenson, J. Am. Chem. Soc. 63, 37 (1941).

<sup>&</sup>lt;sup>10</sup> L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1948). <sup>11</sup> W. Gordy and W. J. O. Thomas, J. Chem. Phys. 24, 440

<sup>(1956)</sup> 

 <sup>&</sup>lt;sup>12</sup> R. M. Badger, J. Chem. Phys. 3, 710 (1935).
 <sup>13</sup> J. H. E. Jeffes, F. D. Richardson, and J. Pearson, Trans. Faraday Soc. 50, 364 (1954).

<sup>&</sup>lt;sup>14</sup> H. Wiedemeier, Z. Anorg. Allgem. Chem. 326, 225 (1963-1964).

A minor attempt was undertaken to measure temperature coefficients of ion intensities from which heats of vaporization of neutral precursors might be deduced, but the results were inconsistent with known properties of the system and were not useful. The difficulties probably arose from progressive temperature errors which are more important in second-law than in thirdlaw measurements. The associated slight trend in the third-law values is revealed in Table II.

# MnS and Graphite System

In the experiments with MnS and graphite, the detection of carbon monosulfide at mass 44 was hindered by a permanent  $CO_2$  background pressure in the mass spectrometer. The detection of CS was therefore based on the presence of C<sup>34</sup>S at mass 46. According to the <sup>34</sup>S abundance in natural sulfur which was used for the preparation of MnS, the isotopic ratio of C<sup>32</sup>S:C<sup>34</sup>S is close to 23:1.

The lower temperature limit at which CS at mass 46 was detectable with certainty was about 1200°C. At 1400°C the mass peak 46 was by a factor of 10 more intense than adjacent hydrocarbon peaks. The intensity of this peak 46 was decreased by more than 95% of its total intensity when the shutter was closed.

An exact determination of the Mn:C<sup>34</sup>S ratio by means of straight collector measurements was not possible owing to the increased noise level under these conditions, but the intensities showed that Mn and C<sup>32</sup>S were of equal importance in the gas phase within a factor of 2. These observations are in good agreement with previous analytical results,<sup>1</sup> which revealed that the composition of the gas phase in equilibrium with MnS-C mixture was Mn:S:C=1:1:1 within limits of error.

The negligible degree to which Reaction (1) occurs in the presence of carbon was shown by the massspectrometric observation that at higher temperatures the  $S_2$  intensity over pure MnS(s) is approximately 25 times higher than over MnS and C. At the same time the Mn intensity is greatly increased by the presence of carbon.

## **Minor Species**

Very approximate values for the energies of dissociation of one sulfur atom from  $MnS_2(g)$  and  $MnS_3(g)$ were obtained from all-gas reactions and the monatomic sulfur pressure to be 76±15 and 86±15 kcal/mole, respectively. The uncertainties in these values are large because of the very low intensities and possible fragmentation at the large electron energies used. Similar calculations for the sulfur polymers based on the very low intensities did not yield equilibrium constants in agreement with those of Berkowitz and Marquart,<sup>3</sup> ours being much lower than theirs. The ions responsible for the signals at masses 110 and 165 might be  $Mn_2^+$  and  $Mn_3^+$ , but their identification was not proved.

## DISCUSSION

The original purpose of the investigation was to reveal through mass analysis the mode of vaporization of MnS itself and of MnS in the presence of graphite, and this goal has been accomplished. In the former case, the predominant reaction is (1). In the latter case, the principal reaction is (2). Thus, the measurements of Wiedemeier and Schäfer<sup>1,2</sup> were correctly interpreted.

New results have been obtained through the massspectrometric third-law studies of reactions involving only gases. The actual pressures were established through intensity ratios obtained with low-energy electrons and the actual pressure of Mn(g) measured previously.<sup>2</sup> Such reactions minimize possible errors that might arise from lack of equilibrium between solids and gases, and the third-law treatment minimizes temperature dependent errors. The results are embodied in the equations,

$$MnS(g) = Mn(g) + S(g),$$
  
$$D_0 = 71 \pm 4 \text{ kcal/mole}, \qquad (4)$$

 $MnS(s) = MnS(g), \quad \Delta H_0^{\circ} = 116 \pm 6 \text{ kcal/mole}, (5)$ 

$$Mn(s)+S(rh)=MnS(g),$$

$$\Delta H_0^{\circ} = 67 \pm 6 \text{ kcal/mole,} \quad (6)$$

These values are based on the pressure of Mn(g) actually measured in previous Knudsen effusion measurements<sup>2</sup> corresponding to the equation,

$$MnS(s) = Mn(g) + \frac{1}{2}S_2(g),$$
  

$$\Delta H_{298}^{\circ} = 137.2 \text{ kcal/mole,} (7)$$

and on the reactions,

$$S_2(g) = 2S(g),$$
  $D_0 = 101 \text{ kcal/mole},$  (8)

$$Mn(s) = Mn(g), \qquad \Delta H^{\circ}_{298} = 69.3 \text{ kcal/mole,}$$
 (9)

Fragmentation of MnS(g) in the electron-impact process was made apparent at 45 and 70 eV by the slight decrease in the apparent value of  $D_0$ . That MnS(g) is a minor species renders the fragmentation error less important, and it was further reduced by the use of the low-energy electrons.

Colin, Goldfinger, and Jeunehomme<sup>15</sup> have performed experiments at higher temperatures and have reported a value of  $65\pm 5$  for the dissociation energy of MnS in good agreement with the present value. Their lower value may have arisen from additional fragmentation or from their calibration technique.

Among the gaseous metallic sulfides, MnS is of moderate stability, comparable to that of CaS and SrS <sup>16</sup>, more stable than FeS, ZnS, CdS, and HgS <sup>16</sup>, but con-

<sup>&</sup>lt;sup>15</sup> R. Colin, P. Goldfinger, and M. Jeunehomme, Nature 194, 282 (1962). <sup>16</sup> J. R. Marquart and J. Berkowitz, J. Chem. Phys. 39, 283

<sup>&</sup>lt;sup>16</sup> J. R. Marquart and J. Berkowitz, J. Chem. Phys. 39, 283 (1963).

siderably less stable than TiS<sup>17</sup> and US.<sup>18</sup> The dissociation energy of MnO has been obtained by Padley and Sugden<sup>19</sup> as  $96\pm3$  kcal/mole, and thus MnS is less stable than MnO by about 1 eV.

The approximate values for  $MnS_2(g)$  and  $MnS_3(g)$ indicate that the energy required to remove a sulfur atom decreases in the series MnS<sub>3</sub>, MnS<sub>2</sub> and MnS according to 86, 76, and 71 kcal/mole.

<sup>17</sup> H. F. Franzen and P. W. Gilles, J. Chem. Phys. 42, 1033-1038 (1965).

<sup>18</sup> E. D. Cater, P. W. Gilles, and R. J. Thorn, J. Chem. Phys.
 **35**, 608–618 (1961); E. D. Cater, E. G. Rauh, and R. J. Thorn, *ibid.* pp. 619–624.
 <sup>19</sup> P. J. Padley and T. M. Sugden, Trans. Faraday Soc. 55, 905 (1976).

2054-2061 (1959).

The differences between the sulfur polymer equilibrium constants and those reported earlier<sup>3</sup> are probably attributable to the small intensities in the present work. In addition, several differences in experimental procedures could be noted. Agreement on the S2 dissociation equilibrium, which involved major rather than minor species, was obtained, as noted previously.

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# Damping of Waves by Surface-Active Materials

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A theory is presented for the damping of waves on a water surface in the presence of dissolved surfaceactive material. Equations are given which are valid for any wave on any liquid surface, subject only to the condition that the liquid be incompressible and the liquid layer be sufficiently deep. The equations are solved by the method of successive approximations; the first approximation is fully discussed. The resulting first-order equations are used in computing damping coefficients for solutions of surface-active materials, the adsorption of which follows a Langmuir isotherm. The computed damping coefficients depend on surfactant concentration and on frequency, as had already been found in experiments. Extension of the theory to insoluble monolayers is discussed.

# INTRODUCTION

THE damping of waves, or ripples, on a free water L surface is promoted by the presence of a surfaceactive material in the water.<sup>1</sup> Several attempts have been made to explain this effect,<sup>2-7</sup> but at present there is no satisfactory quantitative agreement between experimental results and predictions from the various theories. The purpose of this paper is to present a corrected theory and to show its agreement with experimental results.

The theory for the behavior of surface waves is obtained<sup>8</sup> by solving the hydrodynamic equations for liquid motion, subject to the appropriate boundary conditions. Difficulties experienced in finding the correct solution have invariably been due to the use of an incorrect boundary condition<sup>4-7</sup> for the tangential stress.

The theory presented here is based on the assumption that the properties of water remain unchanged even in the immediate proximity of the surface. The surface itself is Gibbs' surface of tension,9 which has zero thickness and to which all the "excess" properties are attributed. The only way in which such a surface can affect liquid motion is by means of its effect on the local values of the stress-tensor components. In particular, the stress component normal to the surface depends on curvature and surface tension as predicted by the well-known Laplace equation. The tangential stress component, at the surface, equals the surface-tension gradient and is therefore always zero at the surface of a "pure" liquid where no gradient in surface tension can exist. The presence of a surface-active material

<sup>9</sup> J. W. Gibbs, The Collected Works, Thermodynamics (Yale University Press, New Haven, Connecticut, 1957), Vol. I, p. 219ff.

<sup>&</sup>lt;sup>1</sup> A. Pockels, Nature **43**, 437 (1891).

<sup>&</sup>lt;sup>1</sup> A. Pockels, Nature 43, 457 (1891).
<sup>2</sup> O. Reynolds (1880), cited on p. 631 in H. Lamb, Hydrodynamics (Dover Publications, Inc., New York, 1945).
<sup>3</sup> V. G. Levich, Acta Physicochim. URSS 14, 308, 321 (1941).
<sup>4</sup> V. G. Levich, Physicochemical Hydrodynamics (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1962).
<sup>6</sup> R. Dorrestein, Koninkl. Ned. Akad. Wetenschap., Proc., Ser.
<sup>8</sup> E. 56 (250 (1051))

B: 54, 260, 350 (1951).

<sup>&</sup>lt;sup>6</sup> F. C. Goodrich, Proc. Roy. Soc. (London) A260, 481, 490, 503 (1961).

<sup>&</sup>lt;sup>7</sup> R. S. Hansen and J. A. Mann, J. Appl. Phys. 35, 152 (1964). 8 H. Lamb, Ref. 2.