of the three above-named solvents, 0.01–0.03 mg. of water per cc. of the solution in contact with the carbide being the limit at which the formation of a precipitate could be detected. Other tests made by adding a known weight of water dissolved in anhydrous ether showed about the same sensibility. Tests made upon other solvents, in which a blank test showed a trace of water, indicated that the test made with alcohol was less sensitive than with the solvents mentioned above, but more sensitive than with acetone. Ethyl acetate, chloroform and carbon tetrachloride showed about the same sensibility as ether.

Summary.

A qualitative test for water, sensitive to less than 0.1 mg. may be very easily and quickly made by bringing the substance to be tested into contact with calcium carbide in the presence of a solvent for acetylene, which is then decanted or distilled into an ammoniacal solution of cuprous chloride. Nearly all the common organic liquids are suitable for use, if carefully dried. The method is applicable to a great variety of substances and especially to volatile organic compounds. The only compounds known to interfere with the test are the stronger acids and substances, such as hydrogen sulfide, which precipitate cuprous salts from solution.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE FREE ENERGY OF THE VARIOUS FORMS OF ELEMENTARY SULFUR.

BY GILBERT N. LEWIS AND MERLE RANDALL.

Received October 5, 1914.

No other element is known to occur in as many different forms as sulfur. Several solid modifications have been studied, of which we shall, for the present, consider only the familiar rhombic and monoclinic forms, S_R and S_M. Rhombic sulfur, being the stable form at room temperature, will be taken as the standard and will therefore be assumed to possess zero free energy and zero heat content. In the liquid state two distinct substances are present, known as S_λ and S_μ (soluble and insoluble sulfur).[1] In the gaseous state at least four modifications have been studied: S, S_2, S_6 and S_8.

Monoclinic Sulfur.

$S_R = S_M$.—The heat capacity of rhombic sulfur has been determined by numerous investigators.[2] When all their data are plotted the most

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[1] Since this paper was written a third kind of sulfur in the liquid state, S_π, has been described by Aten (*Z. physik. Chem.*, **86**, 1 (1913)). His results do not necessitate any material change in the present calculations, nor do they suffice to warrant us at present in attempting to calculate the standard free energies of the several liquid forms.

[2] Regnault, *Ann. chim. phys.*, [3] **9**, 322 (1843); Kopp, *Trans. Roy. Soc. London*, **155**, I, 71 (1865); Bunsen, *Ann. physik.*, [2] 141, 1 (1870); Dewar, *Proc. Roy. Soc.*

probable values for the heat capacity at various temperatures fall on a somewhat curved line, which, however, may be regarded as straight between 0° and 100°, and expressed by the equation

$$C_p(S_R) = 4.12 + 0.0047T \text{ cal. per gram atom.} \qquad (1)$$

Similarly, the available data[1] for monoclinic sulfur lead to the following equation as the most probable linear expression for the heat capacity between 0° and 100°.

$$C_p(S_M) = 3.62 + 0.0072T \qquad (2)$$

Hence for the reaction considered

$$\Delta\Gamma = \Delta C_p = -0.50 + 0.0025T. \qquad (3)$$

The best value for the heat of transition is probably that of Brönsted,[2]

$$\Delta H_{273} = 77.0,$$

hence by combination with the preceding expression we find[3]

$$\Delta H = 120 - 0.50T + 0.00125T^2. \qquad (4)$$

We may now write the equation for the increase of free energy[4]

$$\Delta F^\circ = \Delta H_0 - \Delta\Gamma_0 T\ln T - {}^1/_2\Delta\Gamma_1 T^2 + IT;$$

or

$$S_M = S_R;\ \Delta F^\circ = 120 + 0.50T\ln T - 0.00125T^2 - 2.820T. \qquad (5)$$

The value of I being determined as follows: The temperature at which the free energy change of this reaction is zero, in other words, the transition point, is given by Tammann[5] as 94.6° and by Reicher[6] as 95.5°. We will take the mean, 95°. We may, therefore, substitute in the preceding equation and find $I = -2.820$, whence $\Delta F^\circ_{298} = 17.5$.

The free energy change at 25° was also found directly by Brönsted[7] who determined the relative solubility of the two forms of sulfur in benzene, in ethyl ether, in ethyl bromide, and in ethyl alcohol. The ratio of the concentration of S_M to that of S_R was found to be 1.27, 1.28, 1.28, and 1.3 in the four solvents, respectively. Since both forms of sulfur were shown by Brönsted to give identical solutions with the formula S_8, the free energy change is given by the equation

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London, **76**, 332 (1905); Forch and Nordmeyer, *Ann. physik.*, **20**, 423 (1906); Wigand, *Z. physik. Chem.*, **63**, 293 (1908); Nernst, Koref and Lindemann, *Sitzb. Kgl. preuss. Akad. Wiss.*, **12**, **13**, 247–261 (1910); Nernst, *Ibid.*, **12**, **13**, 261–282 (1910).

[1] Regnault, *Loc. cit.*; Thoulet and Lagarde, *Compt. rend.*, **94**, 1512 (1882); Wigand, *Loc. cit.*; Nernst, Koref and Lindemann, and Nernst, *Ibid.*

[2] Brönsted, *Z. physik. Chem.*, **55**, 371 (1906).

[3] This equation gives at 95° ΔH = 105, while Tammann, *Ann. physik.*, [3] **68**, 633 (1899) obtained the value 100 at this temperature. See also Lewis and Randall, THIS JOURNAL, **33**, 488 (1911).

[4] Lewis, THIS JOURNAL, **35**, 1 (1913), Equation 32.

[5] Tammann, *Loc. cit.*

[6] Reicher, *Z. Krystallographie*, **8**, 593 (1884).

[7] Brönsted, *Loc. cit.*

$$\Delta F^\circ = \frac{R'T}{8} \ln 1.28.$$

Hence $\Delta F^\circ_{298} = 18.3$, a value nearly the same as that found by the other method, 17.5, which value will be used hereafter.

Liquid Sulfur.

While it is probable that a large number of pure liquids contain two or more molecular species in equilibrium with one another, the case of sulfur is peculiar in that the equilibrium under certain circumstances is established so slowly that it has been possible to demonstrate the existence in the liquid state of the two substances known as S_λ and S_μ, and to determine quantitatively at various temperatures the relative amounts of these two substances (which in all probability have the formulae S_8 and S_6, respectively).[1] We have, therefore, three reactions to consider, involving the formation from the standard rhombic sulfur of pure S_λ, of pure S_μ and of the mixture of the two as they exist together in equilibrium, which may be denoted by $S_{\lambda.\mu}$. Of these only the first and last have been fully investigated.

$S_R = S_\lambda$.—The heat capacity of S_λ is given by the equation[2]

$$C_p(S_\lambda) = 5.4 + 0.005T. \quad (6)$$

Combining this with (1) we have for the reaction,

$$\Delta\Gamma = 1.28 + 0.0003T \quad (7)$$

and

$$\Delta H = \Delta H_0 + 1.28T + 0.00015T^2. \quad (8)$$

ΔH_{373} is[3] 467 and thus $\Delta H_0 = -35$ and

$$\Delta F^\circ = -35 - 1.28T\ln T - 0.00015T^2 + 7.77T. \quad (9)$$

The value of $I = 7.77$ in this equation was obtained as follows: Kruyt[4] found that when rhombic sulfur melts to form pure S_λ the melting point[5] is 112.8°. At this temperature, therefore, $\Delta F^\circ = 0$, and the above equation may be solved for I. From this equation we find $\Delta F^\circ_{298} = 94$ cal.

$S_M = S_\lambda$.—We may make a similar calculation for this reaction. The melting point[6] of S_M to form pure S_λ is 119°. This, together with the heat capacities and heats of transition already used, leads to the equation

$$\Delta F^\circ = -155 - 1.78T\ln T + 0.0011T^2 + 10.60T. \quad (10)$$

Subtracting this equation from (9) gives an equation identical with (5) except that $I = -2.83$ instead of $I = -2.82$.

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[1] Our evidence on the basis of which we attribute the formula S_6 to S_μ, is given in a letter published by Smith and Carson, *Z. physik. Chem.*, **77**, 672 (1911).

[2] Lewis and Randall, THIS JOURNAL, **33**, 476 (1911).

[3] Lewis and Randall, *Ibid.*

[4] Kruyt, *Z. physik. Chem.*, **64**, 513 (1908), where a bibliography of earlier work on the different forms of sulfur may be found.

[5] See also Smith and Carson, *Z. physik. Chem.*, **77**, 668 (1911).

[6] Smith and Holmes (*Z. physik. Chem.*, **42**, 469 (1903)) give 119.25°; Wigand in a later paper gives 118.95° (*Z. physik. Chem.*, **75**, 235 (1910)).

This is not the only way of checking the accuracy of the various numerical data employed. Given the equation for $S_R = S_\lambda$, and the melting points of S_R and S_M, we could have calculated without further data ΔH for $S_M = S_\lambda$, and for $S_R = S_M$, and would have obtained values in close agreement with those which we have used. Or we could have assumed the experimental values of ΔH, and then from either of the melting points the other one could have been calculated, just as the transition point, $S_R = S_M$, can be calculated from (9) and (10) when the two melting points are known.

Besides the melting points when S_R and S_M melt to form pure S_λ, we have also the so-called natural melting points, namely, the temperatures at which the solids are respectively, in equilibrium with $S_{\lambda,\mu}$, the stable mixture of S_λ and S_μ. The natural melting point of S_R is 110.4° (Kruyt,[1] 110.6°; Smith and Carson,[2] 110.2°). The natural melting point of S_M[1] is 114.6°. From either of these experimental points we may calculate the free energy of the equilibrium liquid, or with the known data for the heat content of the various forms we may, from the first of these points, calculate the second point, and this calculation gives a value within 0.2° of the one experimentally determined.

$S_\lambda = S_{\lambda,\mu}$.—There is still another way of calculating the free energy of the equilibrium liquid, $S_{\lambda,\mu}$. With decreasing temperature the equilibrium liquid becomes more and more nearly pure S_λ. It would therefore be a very close approximation to the truth to assume that at 25° the free energy of $S_{\lambda,\mu}$ is equal to that of S_λ; or, better, since by extrapolation from data about to be mentioned we find the amount of S_λ converted into S_μ at 25° to be about 0.8%, we may assume that in this very dilute solution the activity of the S_λ is proportional to its mol. fraction, and thus we find by a very simple calculation that $\Delta F^\circ_{298} = -0.8$ cal.

Next from the thermal data it is possible to calculate the free energy of $S_{\lambda,\mu}$ at higher temperatures. In this case, however, the use of the thermal data cannot be made conveniently in the ordinary way, for, as we have shown in the paper dealing with the heat content of sulfur, the specific heat of the equilibrium liquid cannot be expressed as any simple algebraic function of the temperature. We must therefore go back to the fundamental free energy equation which we may write in the form

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

or, when integrated between two temperatures, T_1 and T_2,

$$\frac{\Delta F_2}{T_2} - \frac{\Delta F_1}{T_1} = \int_{T_1}^{T_2} -\frac{\Delta H}{T^2}\,dT.$$

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[1] Kruyt, *Loc. cit.*

[2] Smith and Carson, *Z. physik. Chem.*, 77, 661 (1911).

Now, if $\Delta H/T^2$ is plotted against T, we may perform the indicated integration graphically and thus obtain the free energy at one temperature when it is known at some other temperature. This is the general method which must be employed when the heat of reaction is known at various temperatures, but cannot be conveniently expressed in terms of a simple equation.

The value of ΔH in the formation of 32 g. of S_μ from S_λ we have shown to be 416 cal. The specific heat of S_μ is unknown, but we shall make no serious error in assuming that it is approximately the same as that of S_λ, and therefore ΔH for $S_\lambda = S_\mu$ is approximately constant, and ΔH for $S_\lambda = S_{\lambda,\mu}$ is simply $416x$ where x is the fraction of S_μ in $S_{\lambda,\mu}$. Substituting this value for ΔH in the above equation, we have only to integrate $-416x/T^2dT$. Now from the data of Smith and Holmes[1] and of Carson[2] (see Fig. 1, Lewis and Randall)[3] we have plotted the values of x/T^2 between 25° and 445° and determined graphically the area of this curve between 25° and various upper temperature limits, thus obtaining the following table, in which the first column gives the absolute temperature, the second the fraction of S_μ, the third the value of the integral, and the fourth the value of $\Delta F°$ at each temperature provided that $\Delta F°_{298} = 0$:

TABLE I.

T.	x.	$\int_{298}^{T} -\frac{416x}{T^2}dt$.	$\Delta F°$.
298	0.008	0.0	0.0
373	0.031	—0.00465	— 1.7
393	0.040	—0.00664	— 2.6
413	0.055	—0.00902	— 3.7
423	0.067	—0.01037	— 4.4
433	0.111	—0.01217	— 5.3
443	0.187	—0.01553	— 6.9
453	0.225	—0.01981	— 9.0
473	0.270	—0.0295	—14.0
510	0.313	—0.0496	—25.3
573	0.332	—0.0771	—44.2
653	0.338	—0.1070	—70.0
718	0.341	—0.1267	—91.0

The value of $\Delta F°$ for $S_\lambda = S_{\lambda,\mu}$ at 110.4° can be very readily found from independent data already given, for, this being the natural melting point of S_R, $\Delta F° = 0$ for $S_R = S_{\lambda,\mu}$ and therefore $\Delta F°$ for $S_\lambda = S_{\lambda,\mu}$ is equal to $-\Delta F°$ for $S_R = S_\lambda$. The latter value may be obtained from Equation 9, or, since the interval from this temperature to the point of equilibrium between S_R and S_λ is small, we shall obtain greater accuracy by simplifying the primitive equation

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[1] Smith and Holmes, *Z. physik. Chem.*, 54, 257 (1905).

[2] Carson, THIS JOURNAL, 29, 499 (1909).

[3] Lewis and Randall, *Ibid.*, 33, 476 (1911).

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

to

$$-\Delta H = T\frac{d\Delta F}{dT}$$

and regarding the small temperature interval as an infinitesimal. We thus find at 110.4° for $S_R = S_\lambda$, $\Delta F^\circ = 2.7$, and thus for $S_\lambda = S_{\lambda,\mu}$ $\Delta F^\circ = -2.7$ cal. The value obtained by interpolation in Table I is -2.2 if $\Delta F^\circ_{298} = 0$, or -3.0 if $\Delta F^\circ_{298} = -0.8$, as it was roughly estimated. These calculations have been entered into in more detail than would be warranted by the importance of the particular problem involved, but they afford simple illustrations of the methods which are generally applicable in similar cases.

Gaseous Sulfur.

The next reactions to be considered involve not only much larger free energy changes, but also greater uncertainty in these values. The gaseous phase of sulfur is even more complex than the liquid, and may contain at least four molecular species—S, S_2, S_6 and S_8. We shall attempt to determine the free energy of only one of these, namely, S_2, although the measurements of Nernst[1] on the dissociation $S_2 = 2S$, and those of Preuner and Schupp[2] on the equilibrium between S_2, S_6 and S_8 make it possible to estimate roughly the free energy of the other gaseous forms.

$2S_{\lambda,\mu} = S_2$.—In order to find at the temperature of boiling $S_{\lambda,\mu}$ the difference in free energy between the equilibrium vapor and S_2 at atmospheric pressure (if it could so exist) we will make use of the following device: Let us assume that the equilibrium vapor is expanded reversibly and isothermally to such a low pressure that it is essentially pure S_2, and that then, with the aid, perhaps, of a negative catalyzer, the S_2 vapor is compressed reversibly and isothermally to atmospheric pressure without the formation of any S_6 or S_8. The difference between the values of $\int v dp$ in the two isotherms will be the desired difference in free energy. Now the isotherm of S_2 may be assumed to be that of a perfect gas, that of the equilibrium vapor can be obtained from measurements of the volume of sulfur vapor at different pressures. When we first made this calculation the best available data were those of Biltz and Preuner[3] who determined the density of sulfur vapor at 444.6° between 14 mm. and 458 mm. The relations which they thus obtained between pressure and volume were plotted and the curve extended, as accurately as the data permitted, to one atmosphere on the one side and to 0.0075 atmos-

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[1] Nernst, *Z. Elektrochem.*, **9**, 622 (1903).

[2] Preuner and Schupp, *Z. physik. Chem.*, **68**, 129 (1909).

[3] Biltz and Preuner, *Ibid.*, **39**, 322 (1902).

phere on the other, and the area corresponding to the integral, $\int vdp$, was determined graphically and found to be 97.0 liter atmospheres. Now, assuming that at the lower limit of pressure the sulfur vapor is all S_2, the other isotherm is an equilateral hyperbola coinciding with the first curve at the lower pressures. The corresponding area under this curve was 289 liter atmospheres. The difference of 192 liter atmospheres, or 4650 cal., should be the difference in free energy of the gas S_2 and the liquid $S_{\lambda,\mu}$ at one atmosphere and 444.6°, since the liquid $S_{\lambda,\mu}$ has the same free energy as the equilibrium vapor.

The data from which this calculation was made were subject to considerable uncertainties, which, however, were in part removed by the publication of a more extended investigation on the isotherm of sulfur vapor by Preuner and Schupp.[1] Their results permitted an independent application of the method just outlined. Since these measurements were made at 450°, in order to reduce their results to the boiling point of sulfur a small correction had to be made, details of which need not, however, be given. The final result thus obtained was 4300 cal. We will take as a mean of the two determinations

$$2S_{\lambda,\mu}(l) = S_2(g);\ \Delta F^\circ_{718} = 4500 \text{ cal.}$$

$2S_R = S_2$.—We then have from Equation 9

$$S_R = S_\lambda;\ \Delta F^\circ_{718} = -590 \text{ cal.}$$

From Table I

$$S_\lambda = S_{\lambda,\mu};\ \Delta F^\circ_{718} = -90 \text{ cal.}$$

By combining the three data we find

$$2S_R = S_2 \text{ (g., 1 atmos.)};\ \Delta F^\circ_{718} = 3140 \text{ cal.}$$

In order to find the expression for this free energy change at other temperatures, we must know the heat of the reaction as a function of the temperature. The heat capacity of S_R has been given in Equation 1, that of the gas S_2 will be assumed to be the same as that of oxygen, namely,[2]

$$C_p(S_2) = 6.5 + 0.0010T. \qquad (11)$$

Hence

$$\Delta\Gamma = 1.74 - 0.0084T. \qquad (12)$$

The value of ΔH_0 we may obtain by combining the heat of formation of H_2S from S_2 found by Preuner and Schupp[3] at 1000° with the heat of formation of H_2S from S_R found by Thomsen and Berthelot at room temperature. This calculation, of which the details will be given in the paper on hydrogen sulfide, yields the value $\Delta H_0 = 29600$. We may now make use of the value which we have obtained for ΔF°_{718} and write as the final equation

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[1] Preuner and Schupp, *Z. physik. Chem.*, **68**, 129 (1909).

[2] Lewis and Randall, THIS JOURNAL, **34**, 1130 (1912).

[3] Preuner and Schupp, *Z. physik. Chem.*, **68**, 157 (1909).

$$2S_R = S_2\ (g);\ \Delta F^\circ = 29600 + 1.74T\ln T + 0.0042T^2 - 51.3T, \quad (13)$$

and

$$\Delta F^\circ_{298} = 17600.$$

We wish to express our obligation to the Rumford Fund of the American Academy of Arts and Sciences for financial aid in this investigation.

Summary.

The following table gives the free energy of formation of the forms of sulfur considered in this paper:

TABLE II.

Substance.	F°_{298}.	Equation.	Substance.	F°_{298}.	Equation.
S_R	0	..	$S_{\lambda,\mu}$	—0.8	(Table I)
S_M	17.5	5	S_2	17600	13
S_λ	94	9			

BERKELEY, CAL.

DETERMINATION OF CUPROUS AND CUPRIC SULFIDE IN MIXTURES OF ONE ANOTHER.

BY EUGEN POSNJAK.

Received October 22, 1914.

In the course of an investigation upon copper sulfide minerals, which at the present time is being carried out in this laboratory, it became necessary to discover a method to determine cuprous and cupric sulfide in their mixtures. Such a determination involves great difficulties for the reason that no solvents are known for either of them, *i. e.*, solvents which dissolve them without decomposition. It was therefore necessary to find a substance that would react with only one of the components, or, if reacting with both of them, would yield with each of them a different substance, which in turn could in some way be easily separated and determined.

Several reactions were tried, for instance the oxidation of cuprous sulfide. It is well known that cuprous sulfide changes in an acid solution in the presence of oxygen into cupric sulfide. But experiments showed that this reaction did not stop at cupric sulfide, and that cupric sulfide was also much attacked under these conditions. Finally it was found that the reaction of cuprous and cupric sulfide with silver nitrate offered, under certain conditions, a method for their determination.

The reaction between cuprous sulfide and silver salts has been examined by Heumann,[1] Schneider[2] and more recently by C. Palmer and E. S. Bastin.[3] As a result, this reaction has been expressed by the equation

$$Cu_2S + 2Ag_2SO_4 = Ag_2S + 2Ag + 2CuSO_4$$

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[1] *Ber.*, 7, 1680 (1874).

[2] *Pogg. Ann. Physik.*, 152, 471 (1874).

[3] *Economic Geology*, 8, 140 (1913).