

244. *The Vapour Pressures and Latent Heats of Sublimation of α -, β -, and γ -Sulphur.*

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The temperature coefficients of the rates of effusion of sulphur vapour in equilibrium with (1) α - and β -sulphur over the range 0—60°, and (2) γ -sulphur over the range 0—40°, have been determined by a radiochemical method. The corresponding latent heats of sublimation [cal. mole(S₈)⁻¹] and their 95% limits are: α 23,850 \pm 130; β 23,060 \pm 170; γ 23,110 \pm 180. An approximate determination of the relation between the activities of the effusates and their weights was also made, and values of the vapour pressure of α -sulphur calculated from this agree within experimental error with those of previous workers.

On reasonable assumptions, a further statistical analysis points to a strong probability that the β - and γ -curves intersect at some lower temperature, *i.e.*, that there is a transition point between these two forms.

The effects on the results of allowing for possible partial dissociation of the vapour are discussed, and it is shown that degrees of dissociation consistent with those recently reported for higher temperatures have very small effects.

BRADLEY, HARTSHORNE, and THACKRAY¹ concluded from a consideration of the linear rates of the transformations between α -, β -, and γ -sulphur, and of the temperature coefficients of these rates, that a transition point between β - and γ -sulphur might exist at

¹ Bradley, Hartshorne, and Thackray, *Nature*, 1954, **178**, 400.

some temperature below -18° . We undertook the present work in the hope of obtaining direct evidence for or against such a point, and also to add to the existing vapour-pressure data for the crystalline forms of sulphur. We know of no previous determination of the vapour pressure of γ -sulphur, or of β -sulphur below the α - β transition point.

A modified Knudsen effusion method was used. The sulphur contained a small proportion of ^{35}S (a weak β -emitter, half-life 87 days), and assessments of the relative weights of the effusates, which were collected on a strongly cooled target (silvered internally), were made by measuring their activities by means of a Geiger tube and counting circuit. From these results, values of the latent heats of sublimation of the three forms have been calculated. By an extension of the method an approximate determination of the weight of effusate corresponding to a given activity was also made, and from the result the vapour pressure of α -sulphur at 30° was calculated. This agreed within experimental error with the value obtained by Bradley² at this temperature, using an effusion method and a microbalance technique. From Bradley's value and our relative effusion rates, vapour pressures for all three forms over the temperature ranges of the experiments have been calculated.

Our apparatus was similar to that used by Carson, Stranks, and Wilmshurst³ for determining the latent heat of sublimation of diphenylmercury, but certain improvements and modifications in procedure were introduced.

EXPERIMENTAL

Preparation of the Active Sulphur.—Carrier-free $\text{Na}_2^{35}\text{SO}_4$ solution (obtained from the U.K.A.E.A. Radiochemical Centre, Amersham), equivalent to 2—5 mc, was added drop by drop to 0.5—0.6 g. of inactive "AnalaR" sodium sulphate contained in a platinum boat. The moist mass was dried under an infrared lamp to constant weight, and the boat and its contents were placed in a silica combustion tube. Oxygen-free hydrogen, dried by passage over calcium chloride, was then passed over the sulphate, which was heated to a dull red heat, until the loss of weight approximated to complete reduction to sulphide. The product was dissolved in the minimum quantity of water in a centrifuge tube, which was placed in a rack in a hot-water bath. Iodine in potassium iodide solution was then added drop by drop to oxidise the sulphide to sulphur. Completion of the reaction was marked by a sudden change in the apparent colour of the suspension of sulphur from yellow to white, which was followed after a few minutes by coagulation and precipitation of the sulphur. The sulphur was centrifuged off and washed repeatedly, first with very dilute potassium iodide solution to remove adsorbed iodine, and then with distilled water until the washings were free from iodide ion. It was then dried in a vacuum-desiccator for 24 hr., and finally annealed for 2 days at 90 — 95° to convert it all into S_8 . The method gave yields of 80—90%.

Preparation of Specimens for the Effusion Apparatus.—The specimens of α -, β -, and γ -sulphur for insertion in the effusion cell were prepared as polycrystalline films between pieces of microscope slide, *ca.* $\frac{3}{4}$ in. square, and no. 1 cover slips cut slightly smaller. β - and γ -Sulphur were obtained by inoculating with a cold metal point, and by chilling, respectively, the molten films as described by Hartshorne and others,^{4,5} and the α -films were obtained by allowing the β - and γ -films to transform completely. Before insertion of a preparation in the cell, the cover slip was stripped off. This left almost all the sulphur on the slide. The large surface area thus exposed to the vapour phase was *ca.* 100 times the area of the effusion hole, *i.e.*, much greater than the minimum figure of 10 suggested by Clausing⁶ as necessary to ensure that the equilibrium between the vapour and the solid is not disturbed by the loss of molecules through the hole. (Later work has shown, however, that this effect was not entirely absent; see under "Results" below.) The cover slip was placed in a numbered weighing bottle, and the slide was also placed in this bottle after the run. The exposed film of sulphur was thus protected from contamination when not in use, and the slide and cover slip could be reassembled, and the

² Bradley, *Proc. Roy. Soc.*, 1951, *A*, **205**, 553.

³ Carson, Stranks, and Wilmshurst, *Proc. Roy. Soc.*, 1958, *A*, **244**, 72.

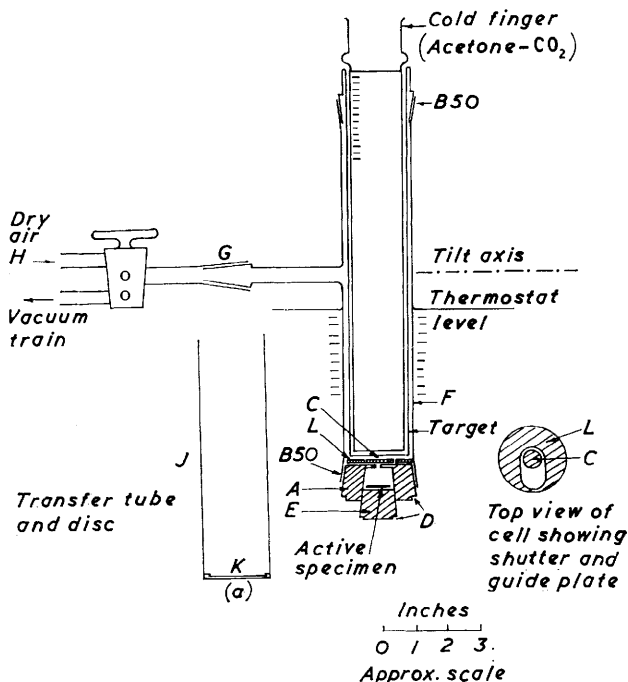
⁴ Elias, Hartshorne, and James, *J.*, 1940, 588.

⁵ Briske and Hartshorne, *Discuss. Faraday Soc.*, 1957, **23**, 196.

⁶ Clausing, *Ann. Physik*, 1932, **12**, 961.

sulphur remelted and treated as above to give a fresh specimen of the β - or γ -form, if required. By examining the β - and γ -films under the microscope, or sometimes even by the naked eye, it was easy to discover whether any transformation to the α -form had occurred. Over the periods of the runs the β -films usually underwent no change at any temperature in the range studied (0–60°), but the γ -films almost invariably began to transform at temperatures above 40°, and so no determinations on this form were made above this point. Preliminary experiments in which β - and γ -films were exposed to strong β -radiation showed that this treatment did not appear to make the films more liable to transform.

FIG. 1.



The duration of a run was chosen to suit the activity of the specimen and the rate of effusion at the temperature in question, and varied from 6–8 hr. at 0° to 10 min. at 60°.

Apparatus and General Procedure.—The effusion cell and target assembly are shown in Fig. 1. The stainless-steel cell *A* was that used by Carson *et al.*,³ but was modified as follows. (1) The upper surface was machined and repolished so as to reduce the thickness of the metal around the effusion hole from the original value of 0.75 mm. to 0.3 mm. (ideally this thickness should be zero). (2) A slotted plate *L* was attached to the upper surface by the minimum quantity of vacuum-grease to form a guide for the disc shutter *C*. (3) Flats *D* were machined on the outer wall and on the tapered plug *E* to fit spanners by means of which the cell could be removed from the outer jacket *F* more easily after a run, and then dismantled.

The cell was inserted in the outer jacket so that the direction of the slot in the guide plate was at right angles to the side tube connecting the apparatus to the vacuum-train. The shutter could then be caused to move so as to cover or uncover the effusion hole by tilting the apparatus slightly about the ground glass joint *G*. The 5-litre thermostat had to be lowered somewhat before this could be done, owing to its small size and the fact that much of its interior was occupied by heating and control apparatus, but this operation was made simple and quick by supporting the thermostat on a counterpoised platform moving very smoothly on rollers and vertical guides. In practice this method of opening and closing the shutter was much simpler and more certain than the magnetic method used by Carson *et al.*

A further modification was the insertion between the effusion apparatus and the vacuum-train of a ground-glass safety valve (similar to the valve on a Töpler pump) to protect the

pumps and McLeod gauge from flooding if the outer jacket of the effusion apparatus should be fractured below thermostat level by the thermal expansion of the metal effusion cell (as happened once). There was a greater danger of this in the present work than in the experiments of Carson *et al.*, because of the higher temperatures to which our determinations were taken. To guard against it, in runs above room temperature the empty cell was always pre-heated in an oven to a higher temperature than that of the experiment to be done, and then after insertion of the specimen was connected to the rest of the apparatus and immersed in the thermostat as expeditiously as possible.

It was found necessary to maintain the cooling of the target tube while it was being transferred to the counting apparatus and throughout the subsequent counting, otherwise the effusate began to evaporate and some condensed on the window of the Geiger tube, giving rise to erratic and valueless results. Since any frost forming over the effusate during these operations would have absorbed the β -radiation, the following procedure was adopted. At the end of a run, dry air was admitted to the apparatus, and the target tube with its cold finger was then withdrawn while a stream of dry air was passed around it from the side tube *H*. As soon as the tube had been raised clear of the outer jacket *F*, the transfer tube *J* (Fig. 1, *a*) was quickly slipped over its lower end, and the lower end of *J*, which was ground flat and slightly greased, was immediately closed with the Perspex disc *K*. *J* made a good sliding fit over the target tube, and *K* was recessed as shown so that it did not foul the effusate.

On arrival at the counting apparatus (Fig. 2) the cooled target tube, still protected by *J* and *K*, was passed through the B 50 socket *M* until its lower end was just above the Perspex box *N* which surrounded the window of the Geiger tube, and through which a stream of dry nitrogen was passed. The disc *K* was then removed and the target tube lowered into position through a circular opening in the top of *N*, as shown in the Figure. The tube *J* was too wide to pass through the opening and remained resting on the top of *N*. The stream of nitrogen was continued throughout the counting.

Traces of frost did form on the target during the transfer to the counting apparatus, since the protection during this operation was not perfect, but these were quickly removed by the nitrogen stream as soon as the target was placed in position in the apparatus.

A reproducible position of the target tube during both effusion and counting was effected by aligning a fixed mark on its B 50 cone with marks on the B 50 sockets into which it fitted on the effusion and counting assemblies respectively.

The counting apparatus consisted of an EHM2S Geiger tube (window thickness 2 mg. cm.⁻²), an Ericsson scaling unit, and an EHT unit (1007).

Counts were corrected for (a) day-to-day variations in the counter sensitivity (determined by means of a standard ¹³⁷Cs source; * see Fig. 2), (b) background radiation, (c) counter paralysis time (300 μ sec.), and (d) decay of the ³⁵S, all counts being calculated as being at the same arbitrary zero time. Counting was repeated a number of times on each effusate to give in most cases a total of at least ~50,000 counts, corresponding to a statistical accuracy (standard deviation) of ca. $\frac{1}{2}$ % (Taylor,⁷ Cook and Duncan⁸). The activity of the effusates obtained at 0° was, however, too low for this total to be reached without making prohibitively lengthy counts, despite the very long effusion runs at this temperature, and totals of 15,000—20,000, corresponding to an accuracy of ca. 1% were the most that could then be conveniently achieved.

Absolute Determination of the Weight of Effusate corresponding to a Given Activity.—A

* This was used because the geometry of the apparatus prevented a source having more nearly the same characteristics as ³⁵S, *e.g.*, ¹⁴C, from being brought near enough to the Geiger tube.

⁷ Taylor, "Measurements of Radioisotopes," Methuen Monographs, 2nd edn., 1957.

⁸ Cook and Duncan, "Modern Radiochemical Technique," Oxford, 1952.

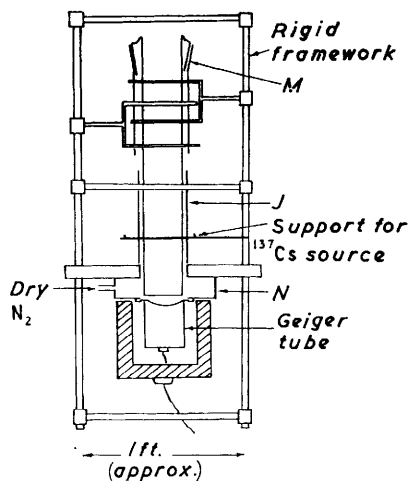


FIG. 2.

specimen of active sulphur was allowed to effuse on to the target and counts were made in the usual way. The target tube and cold finger were then carefully removed from the counting assembly, the transfer tube and Perspex disc (*J* and *K*, Fig. 1) being used to prevent the lower end from frosting. This end was then quickly dipped (after removal of *K* and sliding up of *J*) into a small beaker containing a few c.c. of carbon disulphide and 0.04 g. of inactive sulphur to act as a carrier. The target tube was gently agitated in the carbon disulphide for a few minutes to dissolve off the effusate, rinsed with a little more carbon disulphide, and returned to the counting apparatus, and a count was taken. This showed that over 99.85% of the effusate had been dissolved off the target. The effusate solution was then made up to 25 c.c. in a graduated flask with more carbon disulphide (solution I).

About 1 mg. of the active sulphur was weighed out accurately on a microbalance, transferred to a 1 l. graduated flask together with 3 g. of inactive sulphur as a carrier, and dissolved in carbon disulphide, and the solution made up to the mark (solution II).

A number of aluminium sample pans were modified by machining a recess $\frac{3}{8}$ in. in diameter in their centres. The depths of these recesses and the degree of chamfer of their edges were made as nearly the same as possible.

1 c.c. portion of solution II were pipetted into five of the pans and evaporated to dryness under an infrared lamp. During the last stages of the evaporation the solution collected into a large number of drops, which were led into the recess by means of a drawn-out glass rod. The sulphur finally crystallised in one or two large lumps. These were moistened with acetone and gently crushed with a glass rod. The moist mass was spread as evenly as possible over the recess and finally dried under the infrared lamp.

2 c.c. portions of solution I were pipetted into five other pans and treated similarly.

The amount of carrier sulphur added in making up these solutions was such that the pans in the two sets contained approximately the same weight of sulphur, namely, 3.0—3.1 mg. per pan. Moreover, since the sulphur was spread as evenly as possible over equal areas, self-absorption of the radiation should have been approximately the same for all pans.

The pans were then counted on a standard Geiger counting assembly (not that shown in Fig. 2), variations in the counter sensitivity being checked with a standard ^{14}C source.

From a comparison of the count rates for the two sets of pans with that for the original effusate, the weight of effusate could be calculated, since the weight of active sulphur in solution II was known. From this result the weight of any other effusate obtained with the same specimen of active sulphur could be calculated from its activity, due allowance being made, as always, for decay. The result could, however, only be regarded as approximate, the calculated 95% limits being $\pm 10.8\%$, because the variations in the count rates for the pans were considerable, despite the precautions taken to spread the residues evenly.

RESULTS

The relation between the weight of effusate and the vapour pressure is given by the following modified form of the Knudsen equation,

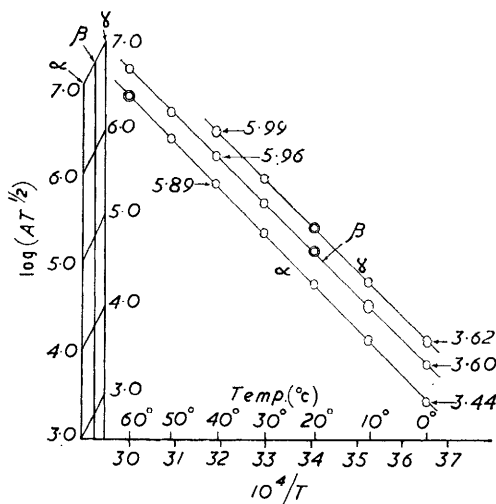
$$G' = atWfp(M/2\pi RT)^{\frac{1}{2}} \dots \dots \dots \quad (\text{i})$$

where G' is the weight of the effusate, a the area of the hole, t the time of effusion, W the Clausing factor correcting for the finite thickness of the cell wall around the effusion hole (which is necessary because some of the molecules moving through the hole strike this wall and are returned to the cell), f a correction factor for the finite distance between the hole and the target, M is the molecular weight of the vapour, and the other symbols have their usual significance. W is given by $1/(1 + l/d)$, where l is the thickness of the wall and d the diameter of the hole, and was 0.753 in the present case. The factor f , which allows for the fact that molecules escaping from the hole at wide angles miss the target, is given by $r^2/(r^2 + h^2)$, where r is the radius of the target, and h the distance between the hole and the target, and was 0.954.

It follows from eqn. (i) that the vapour pressure is proportional simply to the weight of effusate (and thus to the measured activity, A) and to $T^{\frac{1}{2}}$, since all other factors in the equation are temperature-independent. (It is assumed here that M is constant.) Fig. 3

shows the plots of $\log(AT^{\frac{1}{2}})$ against $1/T$ for the three forms. Good straight lines are obtained in all cases. At least two completely independent determinations, and in some cases three or four, were made with each form at each temperature. The maximum difference between the values of $\log(AT^{\frac{1}{2}})$ shown by these determinations was 1.8% (β -form at 10°). In only one other case was the difference greater than 1%, and in the majority it was less than 0.5%. For clarity the distances between the plots have been increased in the figure by shifting the ordinate scale as shown, but qualitatively their positions with respect to one another are correct, *i.e.*, the γ -plot lies above the β -one, and this above the α -one throughout. Values of $\log(AT^{\frac{1}{2}})$ given at each end of the plots indicate the correct spacing. It will be noted that the β -plot lies only slightly above the

FIG. 3.



γ -plot, and there was in fact some overlap of the individual A values for these two forms at 0° and 10° .

The best straight lines and the 95% limits of their slopes (*i.e.*, standard error of slope \times "t" function) were determined by the method of least squares, and correspond to the following values of the latent heats of sublimation [L , cal. mole (S_8) $^{-1}$] to the nearest 10 cal.:

- (1) $L_\alpha = 23,850 \pm 130$;
- (2) $L_\beta = 23,060 \pm 170$;
- (3) $L_\gamma = 23,110 \pm 180$.

(1) may be compared with the value calculated in the same way from Bradley's² results for the range 15.10 – 32.50° , namely, $23,920 \pm 670$. (Bradley in his paper gave a slightly different value for the mean, based on visual assessment of the best slope. The rather large spread of his 95% limits is due to the shortness of the temperature range which his results covered. We are indebted to him for making available to us full details of his experimental results for our calculations.) Neumann⁹ found $24,080 \pm 70$ cal. for the range 59.5 – 90° , and for β -sulphur he obtained $23,240 \pm 70$ cal. for the range 96 – 115° , which may be compared with (2) above. It is not clear from Neumann's paper how his limits of error were evaluated.

A calculation of the vapour pressure of α -sulphur at 30° by means of eqn. (i), G' being obtained from the measured mean activity, and the relation between activity and weight

⁹ Neumann, *Z. phys. Chem.*, 1934, **171**, 416.

of effusate, gives 2.88×10^{-6} mm., if M is taken as 256 ($=S_8$). Recently, however, Cooper and Stranks (personal communication) have shown, from experiments with effusion cells having different sizes of holes, that the error due to the effect of the loss of molecules by effusion on the equilibrium between solid and vapour could not have been negligible for the cell which we used, but must have been about -4% . Allowance for this raises the above value to 3.00×10^{-6} mm. Bradley,² taking the same value for M , found 3.06×10^{-6} mm., and the difference is well within the error of our determination of the relation between activity and weight of effusate (see "Experimental" section). This agreement is reassuring as indicating that our experimental arrangements and procedure were in order.

Table 1 shows the result of taking Bradley's value for α -sulphur at 30° (which we consider to be more accurate than ours, since it was obtained by a more direct method) and calculating the vapour pressures at other temperatures and for the other forms from this and our experimental values of $AT^{\frac{1}{2}}$, using the mean value of A at each temperature. For comparison, vapour pressures of α - and β -sulphur calculated by means of the empirical equations of Bradley² and Neumann,⁹ based on their experimental results, are also given. It must be remembered that Neumann's measurements were made at higher temperatures than ours. He also used a different kind of effusion method in which jets of the vapour issued in opposite directions from two holes in the cell in such a way as to exert a torsional force on the quartz-fibre suspension of the cell. This force, which is what was measured, depends directly on the vapour pressure. *The molecular weight is not involved.* It will be noted that the figures derived from Neumann's equation for β -sulphur agree on the whole more closely with our values for γ -sulphur than with those for β -sulphur, but the difference between the $AT^{\frac{1}{2}}$ values for these two forms is very small, as has already been mentioned. The three sets of figures for α -sulphur agree within a few percent throughout, though Neumann's are appreciably higher than the others at the higher temperatures. These points are discussed at the end of the paper.

The values given above for L_β and L_γ afford no evidence as to whether there is a transition point between β - and γ -sulphur at some lower temperature, *i.e.*, whether their vapour-pressure plots converge in the direction of falling temperature. The figures are so close, and there is so much overlap between their 95% limits, that the difference between

TABLE 1. *Vapour pressures based on Bradley's value for α -sulphur at 30° and the mean $AT^{\frac{1}{2}}$ values of the present authors.*

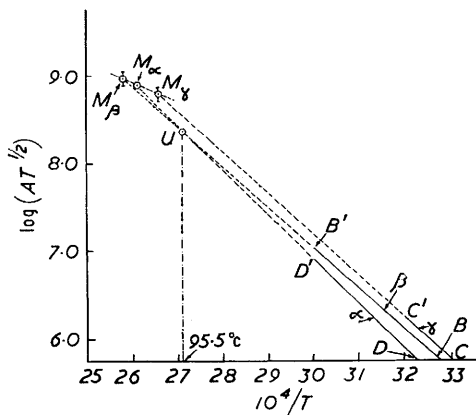
Temp.	Vapour pressure (mm.)					
	α -Form			β -Form		γ -Form
	Bradley's eqn.	Neumann's eqn.	Bradley's eqn.	Neumann's eqn.		
0°	3.81×10^{-8}	3.79×10^{-8}	3.84×10^{-8}	5.61×10^{-8}	5.74×10^{-8}	5.78×10^{-8}
10	1.88×10^{-7}	1.81×10^{-7}	1.84×10^{-7}	2.55×10^{-7}	2.61×10^{-7}	2.68×10^{-7}
20	8.11×10^{-7}	7.72×10^{-7}	7.93×10^{-7}	1.06×10^{-6}	1.07×10^{-6}	1.08×10^{-6}
30	3.06×10^{-6}	3.01×10^{-6}	3.10×10^{-6}	3.71×10^{-6}	3.98×10^{-6}	3.98×10^{-6}
40	1.09×10^{-5}	1.07×10^{-5}	1.11×10^{-5}	1.28×10^{-5}	1.36×10^{-5}	1.35×10^{-5}
50	3.55×10^{-5}	3.53×10^{-5}	3.69×10^{-5}	3.99×10^{-5}	4.35×10^{-5}	
60	1.06×10^{-4}	1.08×10^{-4}	1.14×10^{-4}	1.19×10^{-4}	1.29×10^{-4}	

them is obviously not significant statistically. It must be remembered, however, that they are based solely on the experimental results, without any account being taken of the relation which must exist between the vapour-pressure plots at higher temperatures. These relations are (i) that the plots must meet the plot for liquid sulphur at the respective melting points of the three forms, and (ii) that the plots for α - and β -sulphur must intersect at the α - β transition point. If use is made of these facts, and if it is assumed that the logarithmic plots are straight lines up to the melting points, as seems reasonable in view of the linearity of our graphs in Fig. 3 which cover quite wide ranges of temperature, then a further statistical treatment becomes possible as follows.

The procedure may be followed graphically in Fig. 4, though all the actual results were calculated from the equations of the various straight lines involved. The plotting along the ordinate in the Figure is not to scale, some intervals having been much exaggerated to bring out the procedure more clearly. Only the upper part of the range of temperature covered by the experimental results is represented.

Taking first the upper 95% limit of the slope of $\log(AT^{\frac{1}{2}})$ against $1/T$ for α -sulphur (DD' in the figure), an extrapolation is made to the temperature of the α - β transition point and to the melting point of α -sulphur, giving the points U and M_{α} respectively. The best straight line for the β -form is now calculated by the method of least squares, taking U as the datum point, i.e., the point through which the line must pass, instead of the point given by the means of the experimental values of $\log(AT^{\frac{1}{2}})$ and of the corresponding values of $1/T$ as in the application of the least squares method based on the experimental

FIG. 4.



results alone. This gives $BB'U$ which on extrapolation to the melting point of β -sulphur gives the point M_{β} . The 95% limits of the slope of $BB'U$ are also calculated, and by extrapolation these give upper and lower limits of M_{β} on the ordinate scale, which are indicated by the short horizontal strokes above and below the point in the figure. For each of these three values, i.e., the central value and the two 95% limiting ones, an extrapolation to the melting point of γ -sulphur is made, giving three corresponding points M_{γ} . Each of these is used in turn as a datum point for calculating the best straight line $MC'C$ passing through it and the γ -experimental points, together with the 95% limits of the line. The whole procedure is then repeated, with the lower 95% limit of the α -slope as the starting point. We have thus in all six values for the β -slope covering the whole 95% range of possibilities of the α -slope, and corresponding to each of these six values a range of values for the γ -slope.

The results of applying this treatment are given in Table 2, in terms of latent heats of sublimation.

TABLE 2.

β -Values (cal.)	Corresponding range of γ -values (cal.)	β -Values (cal.)	Corresponding range of γ -values (cal.)
Based on upper α -limit (23,980)		Based on lower α -limit (23,720)	
1. Upper 95% limit...	23,300 23,290—23,400	4. Upper 95% limit	23,130 23,070—23,160
2. Central value	23,230 23,310—23,430	5. Central value	23,010 23,110—23,190
3. Lower 95% limit...	23,160 23,330—23,450	6. Lower 95% limit	22,890 23,140—23,230

The γ -range overlaps the β -value considerably in case 4, and very slightly in case 1, but in all other cases it lies completely above it. Thus the balance of probability appears

to lie heavily in favour of the γ -form's having a greater heat of sublimation than the β -form. This also implies a greater probability that their vapour-pressure curves intersect at some lower temperature than that they do not, *i.e.*, that a transition point exists between them. This transition point would almost certainly have to be below -18° , because Bradley, Hartshorne, and Thackray¹ observed that the interface between the two forms in CS_2 -catalysed sulphur moved in the direction of the disappearance of the γ -form at all temperatures down to this. We cannot of course estimate the actual position of this point from our results.

The temperature taken for the α - β transition point in the above statistical analysis was 95.5° . This appears to be the best mean value of the *direct* determinations of this point which have been made (see Gmelin's "Handbuch der Anorganischen Chemie"¹⁰). For the melting points of α -, β -, and γ -sulphur the "natural" points obtained by Smith and Carson¹¹ were used, namely, 110.2° , 114.5° , and 103.4° respectively. These were chosen out of a number of somewhat varying values in the literature because they are the only determinations made on all three forms by the same authors, and it was considered more important for our purpose that the relative values should be correct, than they should be the best values individually. The "natural" melting points were selected in preference to the "ideal" melting points, because the former refer to an equilibrium condition and their determination is therefore probably the more trustworthy.

Effect of Dissociation of the Vapour.—Bradley's and our values of the vapour pressures given in Table I are based on the assumption that the vapour consists wholly of S_8 molecules, as has already been stated. Braune, Peter, and Neveling¹² have found, however, from a study of the vapour density of sulphur vapour between 120° and 420° at different total pressures, that even at 120° there is considerable dissociation, the vapour in equilibrium with liquid sulphur at this temperature being said to contain 24.4% of S_6 , 0.2% of S_4 , and 0.1% of S_2 . A graphical extrapolation of these authors' results* gives *ca.* 16% for the proportion of S_6 in vapour in equilibrium with liquid sulphur at 0° (our lowest experimental temperature), and the vapour in equilibrium with solid sulphur at this temperature, being at a lower pressure, would on the same basis of calculation contain rather more.

From eqn. (i) we see that the calculated vapour pressure based on a Knudsen effusion experiment is inversely proportional to the square root of the value taken for M . Let us now take the above value of Braune, Peter, and Neveling for S_6 at 120° , rounding it to 25% and ignoring the very small percentages of S_4 and S_2 , as giving approximately the dissociation of sulphur vapour in equilibrium with solid sulphur in the neighbourhood of the melting points of the three forms (where the saturation vapour pressures of solid and liquid would be nearly equal). This corresponds to $M = 240$, while for no dissociation $M = 256$. Thus if we disregard the dissociation, the calculated vapour pressure will be too low by a factor of $(240/256)^{\frac{1}{2}} = 0.97$, or by about 3%. Within the temperature range of our determinations, 0 – 60° , we should expect the proportion of S_6 , and therefore the error, to be less than this.

The effect on the values of the heats of sublimation of ignoring a degree of dissociation of the above order will now be considered. Taking the most unfavourable case possible, let us suppose that in the neighbourhood of the melting points the vapour contains 25% of S_6 , but that the dissociation falls to zero at 0° . If we allowed for this it would increase the values of the latent heats by only *ca.* 0.25%, *i.e.*, 60 cal. Since, on the basis of the extrapolated results of Braune, Peter, and Neveling, dissociation at the lower temperatures would not in fact be so very much less than near the melting points, it may well be that the effect on the values of the latent heats of not allowing for dissociation is negligible.

* Using the logarithms of their saturation partial pressures plotted against $1/T$, which give good straight lines.

¹⁰ Gmelin, "Handbuch der Anorganischen Chemie," 1942–1953, Vol. IX, p. 626.

¹¹ Smith and Carson, *Z. phys. Chem.*, 1911, **77**, 661.

¹² Braune, Peter, and Neveling, *Z. Naturforsch.*, 1951, **6a**, 32.

It is of interest in connection with the above discussion that Neumann's values for α - and β -sulphur in Table 1 are almost uniformly higher than Bradley's and ours, with a tendency for the difference to increase with rise of temperature. The maximum difference, *ca.* 8–9% for β -sulphur at 50° and 60°, is considerably greater than that just estimated for the effect of dissociation, but the difference may be at least partly due to the fact that Neumann's method led directly to the value of the vapour pressure without regard to the value of M , whereas Bradley's and ours did not, and we made no allowance for dissociation.

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