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Dedicated to Prof. Dr. H. J. Seifert on the occasion of his 60th birthday

INVESTIGATION OF THE PHASE BAROGRAMS AND DIAGRAMS OF THE GeI_4-I_2, GeI_4-BiI_3 AND GeI_4-HgI_2 SYSTEMS

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The phase barograms of the systems GeI_4-I_2, GeI_4-BiI_3 and GeI_4-HgI_2 were determined by total pressure measurements in a membrane zero manometer and the resulting phase diagrams were compared with those obtained by DTA measurements. All the systems were single eutectics.

In previous works, the HgI_2-I_2 [1, 2] and the BiI_3-I_2 and BiI_3-HgI_2 [3] phase systems were investigated, and it was stated that the single eutectic systems are very similar, they have nearly ideal melting behaviour and their barograms are of similar structure. We carried on by investigating the GeI_4-I_2, GeI_4-HgI_2 and GeI_4-BiI_3 systems, among them the melting diagram for GeI_4-I_2 is known [4] and, concerning the two others, a single eutectic nature was expected due to the similar molecular structure.

The melting diagram of all three systems were calculated assuming ideal solution behaviour following Raoult's law

$$\log N_A = -\frac{\Delta H_L}{2.303 \cdot R}\left(\frac{T_0 - T}{T_0 \cdot T}\right)$$

where the temperature dependence of the heat of melting ΔH_L with $C_P(T-T_O)$ was taken into account and

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$$\log N_A = -\left(\frac{\Delta H_L - C_p \cdot T_0}{2.303 \cdot R}\right)\left(\frac{T_0 - T}{T_0 \cdot T}\right) + \frac{\Delta C_p}{R} \cdot \log\left(\frac{T}{T_0}\right)$$

was obtained [1, 2], where N_A is the molar fraction of the substance A, ΔH_L the heat of melting, ΔC_P is the molar heat difference, R the gas constant, T_0 the melting temperature of the substance A, and T the melting temperature of the system with a molar fraction of N_A.

GeI_4, BiI_3 and GeI_2 were obtained by direct synthesis from the elements in a closed tube and a two zone furnace (GeI_4 : 750° → 180° ; Bi I_3 : 450° → 180° ; HgI_2 : 225° → 180°) and purified by subsequent sublimation. I_2 was simply resublimated. The substances were stored and put into the membrane zero manometer in small quartz glass ampoules with a bottom drawn towards the interior [2].

1. The GeI_4 - I_2 system

1.1 Total pressure measurements, barogram

From previous investigations of the Ge-I_2 [5] system, the phase diagram of the total system Ge-I_2 on the side rich in Ge was deducible, i. e. in the Ge-GeI_2 and GeI_2-GeI_4 sections, the phase barogram of the GeI_4-I_2 was unknown. The total pressure curves in relation to liquid GeI_4 have been determined repeatedly [5–7], the evaporation curve of iodine is well known; compare [2, 3 and 8].

To measure the total pressure of GeI_4-I_2 mixtures, different GeI_4/I_2 ratios were used so that the total saturation curve along the monovariant three-phase line was ensured to be solid-liquid-gaseous, along the monovariant two-phase lines solid-gaseous and liquid-gaseous, respectively, for the GeI_4 and I_2 boundary phases.

In Fig. 1, the measured pressure-temperature composition data were registered, the result being the phase barogram of the GeI_4-I_2 system.

The total pressure curve of iodine goes up to the melting point S_1 at 114° along the logarithmic $1/T$ straight line (1) and is consistent with previous measurements [2, 3]. At the melting point, 146°, the vapour pressure is about 3.5 torr and, with regard to its course the curve best corresponds to the measurements of Chernyaev *et al.* [6]. Mixing on the eutectic side rich in I_2 – see Fig. 2. – a total pressure course is shown along the I_2 straight line up to nearly above 100° (and afterwards bends, curve 2). At the bending point, the precipitates contain 10 mol% GeI_4. In the case of mixtures, which have a greater GeI_4 content than in consistency with the eutectic, the curves bend at E from the total saturation curve of iodine, pass a pressure maximum and approach the GeI_4 saturation vapour pressure at S_2. At about 130°, the maximum pressure value of the E-S_2 three-phase line is 35 torr. Because of the low iodine content of samples 6 and 8, the pressure curve does not completely pass the three-phase line, but it deviates from the saturation curve and until meeting it again goes on at higher temperature with a smaller slope. For samples 3–8 the bending points from the three-phase line correspond to the melting temperatures of the really existing

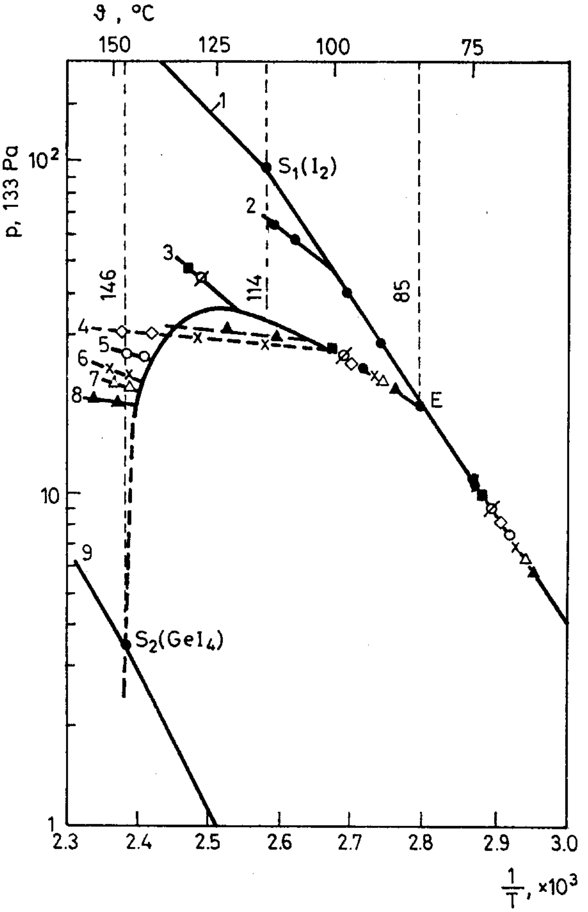

Fig. 1 Phase diagram of $GeI_4 - I_2$ system Mole per cent: 1 – I_2; 2 – 10; 3 – 60; 4/5 – 88; 6 – 90; 7 – 92.8; 8 – 93; 9 – GeI_4

precipitate compositions indicated in Fig. 1 (description of the figure). The melting points obtained are registered in Fig. 2.

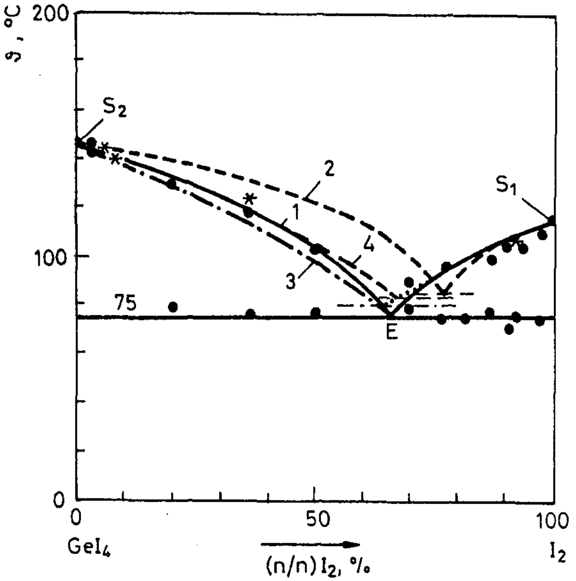

Fig. 2 Melting diagram for the GeI_4-I_2 system; 1 – DTA curve; 2 – Maneglier *et al.* [4]; 3, 4 – calculated with ΔH_L = 4.61 kcal/mol or 5.35 kcal/mol
* – from total pressure measurements, Fig. 1

It is remarkable that during the cooling process the course of three-phase line cannot be explained in spite of the long temperature holding times. At low temperatures, only pressures along the saturation vapour pressure of iodine were measured. This phenomenon indicates a supercooled melt. When heating these mixtures again, the course along the three-phase line is observed.

Because of the comparatively low total pressure of the three-phase line, slight inaccuracies in the determination of pressure -temperature value pairs result in relatively high deviations in the melting temperature of the relevant precipitates.

1.2 Calculation of the GeI_4-I_2 melting diagrams

Proceeding from the relations mentioned, the liquidus lines for the boundary phases GeI_4 and I_2 were calculated. As heat of fusion for GeI_4, the value of 4.61 kcal/mol (19.3 kJ/mol) [5] and 5.35 kcal/mol (22.4 kJ/mol) [5] were applied and, for iodine 3.77 kcal/mol (15.8 kJ/mol) [10]. The melting temperatures are 146° (419 K) for GeI_4 and 114° (387 K) for iodine. The medium molar heat difference of the liquid and solid for GeI_4 is ΔC_P = 4.2 cal/k·mol (17.6 J/k·mol) [11–13], for details see [14].

The liquidus lines for GeI_4 calculated from both values of heat of fusion are indicated in Fig. 2. Accordingly, the eutectic composition should be at 36 or 32% (n/n) GeI_4. The eutectic temperature is determined as 80° (353 K) to 85° (358 K).

1.3 Differential thermal analysis–melting diagram

As already described [9], the differential thermal investigations were carried out using a modified DTA apparatus. DTA ampoules were made using Rasotherm glass with a thin bottom of these ampoules was drawn towards the interior of the ampoule. For the measurements, each time 100 mg of the mixture was weighed, put into the ampoule and melted in vacuo. The heating rate was 5 deg/min. In Fig. 3, as an example, the curve is shown for a mixture containing 12.7% (n/n) of GeI_4 and 87.3% (n/n) of I_2. As the eutectic temperature, the intersection point of the extrapolated base line with the steepest slope of the peak was used. Melting temperatures were read at the

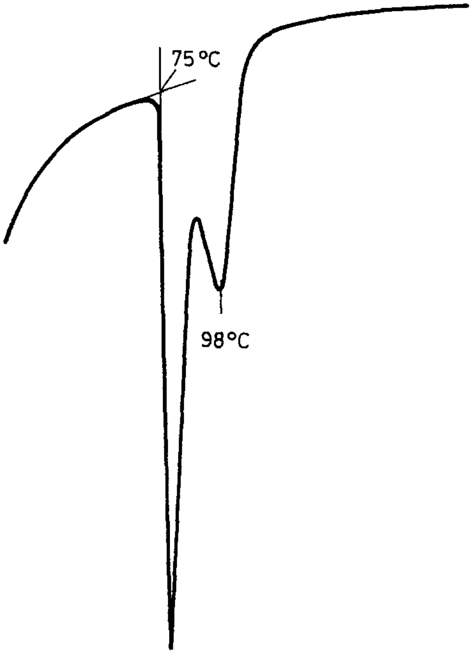

Fig. 3 Example of a DTA curve taken for the GeI_4-I_2 system for 12.4% GeI_4

maximum of the melting peak. In Fig. 2, the composition-temperature data pairs are indicated. Temperature values of the eutectic vary around the average 75° (348 K) ± 2.5°. The eutectic temperature indicated in the barogram is about 5–10° higher. The calculated value also rose to the same extent. By extrapolation at 34% (n/n) GeI_4, the eutectic composition is obtained.

The curve (cf. 1. 2.) coincides with that determined by DTA.

It can be concluded from the curves determined that the particles do not interact significantly and show a nearly ideal behaviour.

No thermal effects were indicated on the cooling curves which means that a considerable supercooling took place, as it was observed for total pressure measurements over GeI_4-I_2 precipitates.

Melting temperatures determined by the barogram (Fig. 1) fit into the melting behaviour determined by DTA. The liquidus lines indicated by Maneglier *et al.* [4] deviate from that determined in this paper.

2. The GeI_4-BiI_3 system

2.1 Total pressure measurements, barogram

Assuming ideal behaviour, an eutectic in the vicinity of the GeI_4 boundary phase was expected (see 2.2.). With the mixtures, until the eutectic temperature (*E*) the pressure values were measured to be along the saturation pressure line of GeI_4. The temperature of the bending point *E* was determined as 143° (416 K). With further temperature increase,the pressure values measured were only slightly below the saturation curve of GeI_4 (see Fig. 4). The maximum of the E-S_2 three-phase line could not be exactly registered, as this range was only slightly above 760 torr and thus, beyond the measuring range. However, in realizing the experiment, it was ensured that the pressure maximum was about 385° (658 K) and did not exceed 950 torr; (curve 2, Fig. 4). Sample 3 was mixed in such a way that in the temperature range between 335° (608 K) and 400° (673 K) the three-phase line was "tunnelled", i. e. the total pressure did not correspond to saturation and, only above 400°, went along the three-phase line towards S_2. The bending points to be assigned to the melting temperature were at 403° (676 K) and 4.1% (n/n) GeI_4 and 408° (681 K) and 2.2% (n/n) GeI_4.

Total pressure measurements show that the system is single eutectic, i. e. there is neither a compound formation nor a miscibility gap. The extreme position of the three-phase line could be explained by assuming great repulsive forces between BiI_3 and GeI_4.

2.2 *Calculation of the GeI_4-BiI_3 melting diagram*

In calculating the liquidus line of the BiI_3 boundary phase by the equation mentioned at the beginning, the following values were taken: for BiI_3 the heat of fusion, 10 kcal/mol (41.9 kJ/mol) [15] and 7.6 kcal/mol (31.8 kJ/mol) [10], respectively. The molar heat difference ΔC_P (BiI_3, liquid-solid) was estimated as 2.5 cal/k·mol (10.5 J/k·mol). This was done following the trihalide values of Barin and Knacke [8]. The melting temperature used was 408° (681 K).

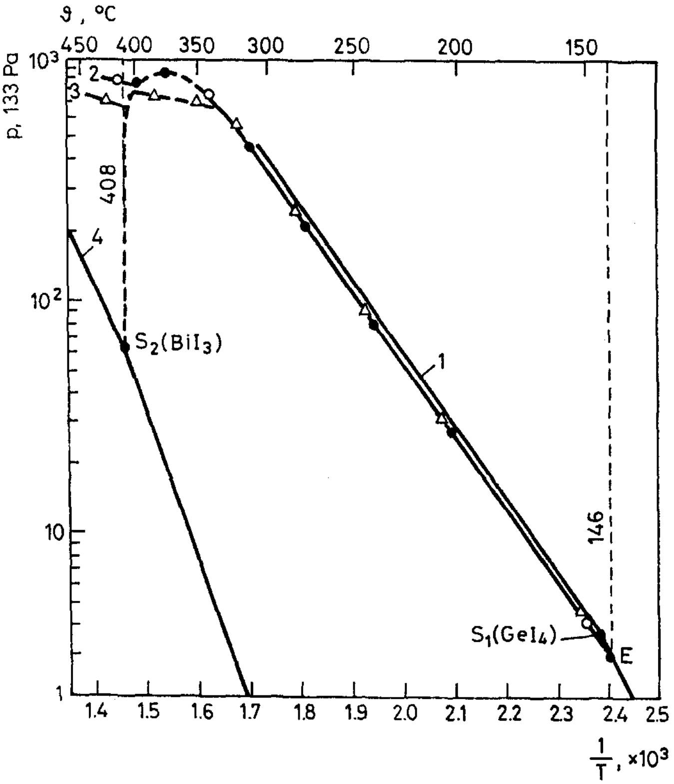

Fig. 4 Phase barogram of the GeI_4-BiI_3 system Mole per cent GeI_4: 1 – GeI_4; 2 – 4.1; 3 – 2.2; 5 – BiI_3

The liquidus lines calculated in this way are shown in Fig. 5. Hence, the eutectic temperature has values which are only slightly below the melting

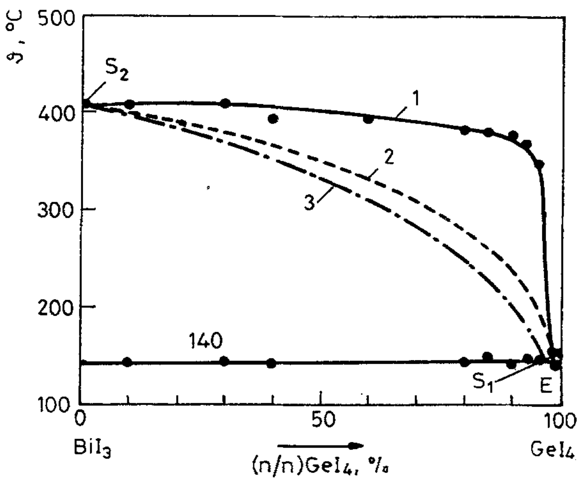

Fig. 5 Melting diagram for the system GeI_4-BiI_3; 1 – DTA; 2 – calculated with ΔH_L = 10 kcal/mol; 3 – calculated with ΔH_L = 7.67 kcal/mol
* – from total pressure measurements, Fig. 4

temperature of GeI_4; between 140° (413 K) and 145° (418 K). The eutectic would be between 1% (n/n) GeI_4 and 4% (n/n) GeI_4. The various values for the heat of fusion lead to various melting temperature-molar fraction data pairs in the medium molar fraction range; with regard to the eutectic, there are nearly the same consequences.

2.3 Differential thermal analysis, GeI_4-BiI_3 melting diagram

In analogy with the previous system, weighed portions of 100 mg of the respective GeI_4 and BiI_3 mixtures were heated at a rate of 5 deg/min. The results are indicated in Fig. 5. The system is a single eutectic, the eutectic is at 97% (n/n) GeI_4 and 140° (413 K) ± 2.5°. The coordinates determined by DTA for the eutectic coincide with those determined by calculation. The liquidus line determined by DTA is far beyond that determined for BiI_3. This is explained by a considerable interaction between BiI_3 and GeI_4 as has already been concluded from the extreme course of the three-phase line in the pressure measurements (cf. 2. 1., Fig. 4). The sharp decline of the melting curve towards the eutectic point is in agreement with the steepness of the three-phase line and the related pressure maximum in the barogram.

3. The GeI_4-HgI_2 system

3.1 *Total pressure measurements, barogram*

The phase barogram of the GeI_4-HgI_2 system shows a special feature, e. g. both boundary phases have nearly the same vapour pressure.

To describe the phase barogram (Fig. 6), three weighed portions were selected, one on the right side of the eutectic, two on the left side of the eutectic with a high content of HgI_2. Sample 2 in Fig. 6 shows a pressure course along GeI_4 saturation curve up to nearly 145° (418 K) and afterwards it is lower. The real solid composition at the bending point is 1% (n/n) HgI_2. In the initial range, the total pressure of samples 3, 4 and 5 is lower than the GeI_4 saturation vapour pressure (curve 1), however, it increases more steeply and intersects the vapour pressure curve of GeI_4 near 175° (448 K), at about 11 torr. Until the pressure maximum of about 120 torr at 245° (518 K) is reached, the three-phase line *E*-S_1 goes along above the saturation vapour pressure curve (1) and afterwards, steeply declines to the melting point S_2

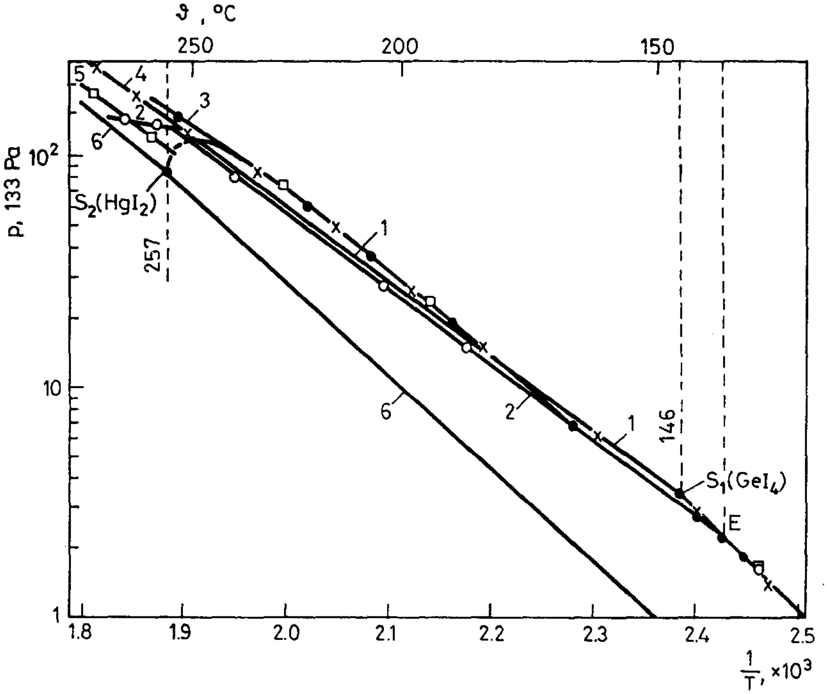

Fig. 6 Phase barogram of the GeI_4-HgI_2 system
Mole percent: 1 – GeI_4; 2 – 99; 3 – 39; 4 – 9; 5 – 4; 6 – HgI_2

of HgI_2 at 80 torr (curve 5). Samples 3 and 4 leave the three-phase line at 237° (510 K) with 39% (n/n) GeI_4 and 248° (521 K) and 9% (n/n) GeI_4, sample 5 at 4% (n/n) GeI_4 and 254°.

3.2 Calculation of the melting diagram for GeI_4-HgI_2

The course of the liquidus line on the side rich in GeI_4 is taken from 1. 2. To calculate the liquidus line of the side rich in HgI_2, the heat of fusion ΔH_L equal to 4.53 kcal/mol (19 kJ/mol) [1], the molar heat difference ΔC_P of 4.8 cal/k·mol (20.1 J/k·mol) [1, 10] and the melting temperature of 257° (530 K) were used; cf. [2].

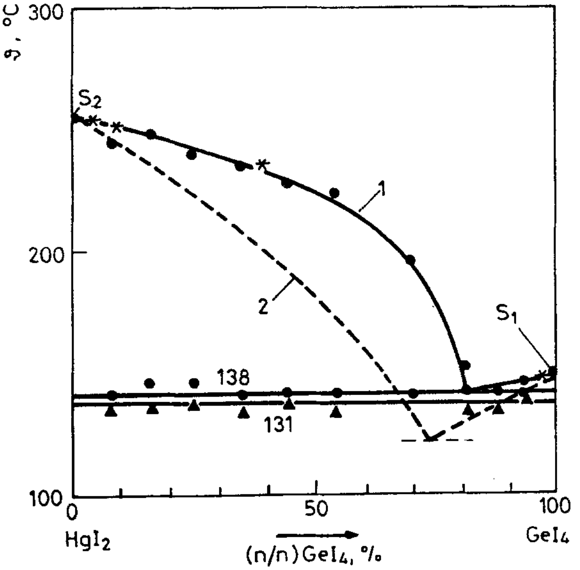

Fig. 7 Melting diagram for the GeI_4-HgI_2 system; 1 – DTA; 2 – calculated with ΔH_L = 4.53 kcal/mol;
* – from total pressure measurements, Fig. 6; **– limit of solubility of GeI_4 in HgI_2

The calculated molar fraction-temperature pairs are indicated in Fig. 7. The coordinates of the eutectic point, following these calculations, should be 122° (395 K) and 73% (n/n) GeI_4.

3.3 Differential thermal analysis, melting diagram of GeI_4-HgI_2

The thermal effects determined are indicated in Fig. 7. In addition to signals at the eutectic and melting point, a third signal was recorded at 131.5°

(404 K), which is assigned to the α, β phase transition of HgI_2 [15, 2]. By means of the behaviour determined by DTA, the eutectic temperature of 138 ± 2.5° (411 K) and the eutectic composition of 82% (n/n) GeI_4 can be determined. Compared with the values calculated, the experimental values are considerably higher. The behaviour of the liquidus lines determined by DTA is confirmed by the results of the total pressure measurements. Both experimentally determined liquidus lines take a course above the calculated one. Hence, it may be concluded that in this system, too, no ideal solution behaviour is observed and interactions occur.

3.4 Solubility of GeI_4 in solid HgI_2

With regard to the optoelectronic properties of HgI_2 [16], mainly the solubility of metal iodides of other valences is of interest. To determine the solubility limit of GeI_4 in HgI_2, HgI_2 crystals were thermally treated beside GeI_4 as illustrated in Fig. 8. Quartz ampoules standing vertically in a two-zone furnace were exposed to a temperature gradient of 225° (498 K) to 190° (463 K) for several days. A constant amount of HgI_2 was used and the quantity of GeI_4 was varied. According to the limit of solubility it was expected that GeI_4 dissolved in HgI_2 and the excess GeI_4 should remain in the gas phase or as a condensation product. The recrystallized and doped HgI_2 crystals were analyzed by mass spectrometry.

For three different weighed portions of GeI_4 with 50 mg and 120 mg and 500 mg HgI_2 in each case a percentage of 0.04, 0.06 and 0.05 (n/n) GeI_4 was

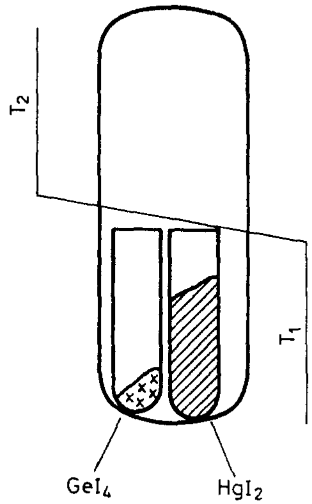

Fig. 8 Experimental arrangement to dope HgI_2 with GeI_4

identified in the HgI_2 crystals. Hence, the limit of solubility of GeI_4 in HgI_2 is about 200° at 0.05 ±0.02 mole per cent.

4. Discussion of the results

Among the three systems investigated, the GeI_4-I_2 system shows a nearly ideal solution behaviour. Hence, it resembles the HgI_2-I_2 [1, 2] and BiI_3-I_2 [3] systems. For these systems the phase barogram is similar since iodine has a much higher volatility than GeI_4, but the three-phase line takes a flat course and has its maximum where GeI_4 has a vapour pressure of only some torr. The forces of attraction of molecules are equal.

The melting diagram and the phase barogram of the GeI_4-BiI_3 system deviate considerably from the ideal solution behaviour. This deviation consists in the steep course of the three-phase line, which in the initial range is nearly identical with the saturation vapour pressure curve of GeI_4. The saturation vapour pressure of BiI_3 is already some torr, interaction forces are indicated, for which the relation

$$A\text{–}A \gg A\text{–}B \ll B\text{–}B$$

is valid and, which become as effective as the repulsive forces.

The GeI_4-HgI_2 system is similar to the previously described system BiI_3-GeI_2, but the phase barogram of this system is of a completely different shape because the saturation pressures are more similar. The fact that the three-phase line intersects the GeI_4 saturation curve at about 175° and 10 torr and that the maximum is only at 250° (523 K), where the saturation pressure if HgI_2 is already 70 torr, is in accordance with the considerable deviation of the liquidus line deviating from that determined by Raoult‘s equation.

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Zusammenfassung — Durch Gesamtdruckmessungen mittels eines Membrannullmanometers wurden Phasenbarogramme der Systeme GeI_4-I_2, GeI_4-BiI_3 und GeI_4-HgI_2 ermittelt und die resultierenden Phasendiagramme mit den an Hand von DTA-Messungen erhaltenen verglichen. Alle diese Systeme besitzen einen eutektischen Punkt.