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Design, Construction and Testing of a Heat of Vaporization Calorimeter useful in the Vapor Pressure Range 1 to 0.01 mm Hg at 25° C

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A method for the experimental determination of heats of vaporization at 25° of substances exerting a vapor pressure in the range 10 to 10^{-3} mm Hg has been developed. A micro-calorimeter was constructed in the form of a Knudsen cell from which the substance was evaporated into high-vacuum. With a charge of *ca.* 300 mg of sample usually 5 to 8 consecutive experiments were performed. The vaporization heat was electrically compensated.

The even-numbered alkanes from octane to hexadecane served as test substances. A further control was obtained by measuring heats of vaporization of propyl disulfide and benzenethiol. Heat of sublimation and vaporization values were determined for solid and liquid samples of phenyl diacetamide, and the difference was compared with the experimentally determined heat of fusion.

The reproducibility was found to be satisfactory in the whole pressure range; however, a systematic error impaired the experimental data. A correction could be applied in the pressure range $10-10^{-2}$ mm Hg. It is believed that, at present, the accuracy of the corrected results is at least 0.1 kcal.mole^{-1}. At a vapor pressure of 10^{-3} mm the error was found to be as much as 2–3 kcal.mole^{-1}. It is likely that this discrepancy is due to the existence of a residual pressure close to the evaporation cup of the same order of magnitude as the vapor pressure of the substance.

By designing a more effective pumping system it is assumed that heats of vaporization of substances having a vapor pressure down to 10^{-3} or even 10^{-4} mm will be accessible for determinations with an improved method.

Experimental determinations of heats of vaporization (ΔH_v) at the standard reference temperature, 25°C, of substances having fairly low vapor pressures are very scarce in the literature. Either the heat of vaporization has been determined at higher temperatures and the value at 25°C obtained from additional specific heat measurements, or vapor pressure data at different tempera-

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tures have been used to calculate ΔH_v (25°) using Clausius-Clapeyron's equation. In most cases, however, only empirical rules are available for a rough estimation of ΔH_v.

The method of determining ΔH_v at higher temperatures together with specific heat measurements is capable of yielding very accurate values, the standard deviation being only at few thousands of a kilocalorie per mole. However, the method is time-consuming and usually requires from fifty to several hundred grams of substance, which limits its use to compounds available in large quantities. Besides, this method has so far been used only at vapor pressures above *ca.* 20 mm.

The use of Clausius-Clapeyron's equation requires reasonably accurate vapor pressure data, which must be carefully evaluated owing to the frequent presence of systematic errors inherent in the method.

Recently, Wadsö[1] developed a method for the direct determination of $\Delta H_v(25°)$ in which he used a carrier-gas technique. Within the boundaries of a calorimeter system a flow of nitrogen or argon was forced to pass above the surface of a 200 mg - sample of the substance and it was thereafter thermally equilibrated, the vaporization heat being electrically compensated. This method has been shown to give accurate results to within 0.02 kcal per mole for substances having vapor pressures in the range 150 to *ca.* 1 mm of Hg. At the lower pressure end zero-effects started to influence severely the accuracy of the measurements.

Nevertheless, the good results obtained with the calorimeter stimulated a study of the possibilities for the development of a calorimeter that would be suitable for the direct determination of $\Delta H_v(25°)$ for substances exerting pressures in the range of 1 to 0.01 or preferably 0.001 mm Hg.

GENERAL CONSIDERATIONS

The carrier-gas technique. It seemed to be impractical to extend the use of the carrier-gas technique to the required low-pressure region for the following main reasons.

The aforementioned zero-effects, which are caused both by nonideality of the carrier-gas as well as by friction between the gas and the walls of the passage, depend on the whole on the pressure drop of the carrier gas within the calorimeter boundary. This pressure drop between the gas inlet and outlet tubes is governed by such factors as length, area and geometry of the gas passage, the absolute gas pressure and the velocity of the streaming gas. In order to suppress the zero-effects it is therefore necessary to increase the size of the gas passage and to have a very simple design. This means inevitably that the size of the calorimeter must be considerably increased compared to that of Wadsö's calorimeter.

As the vapor pressure of the substance decreases it is further necessary to increase the amount of carrier gas passing over the surface of the sample in order to achieve a reasonable rate of vaporization. This again leads to an increased size of the calorimeter.

Now, the amount of substance that can be expected to vaporize in the lowest pressure region is of the order of 10 mg, which quantity should be determined with an accuracy of preferably 1 in 5000. These conditions put a severe restriction on the size as well as the weight of the calorimeter. It was felt that the method of freezing-out and weighing the vaporized amount outside the calorimeter system introduced even more pronounced difficulties from a constructional as well as an operational point of view. This method was therefore not seriously considered. Thus, the requirement was set that the part of the calorimeter containing the substance must not weight more than *ca.* 15 g to permit the use of an ordinary micro-balance with a maximum load of 20 g.

These considerations led to the conclusion that the carrier-gas technique must be abandoned and it was felt advisable to simplify the constructional problems as much as possible and to start the development of the method by building a simple evaporation chamber from which the vapor of the sample could escape through an opening into a high-vacuum system.

Evaporation into a vacuum. The problems met in applying this technique are partly common to those inherent in many methods for the determination of low vapor pressures, all of which principally make use of a Knudsen cell. Additional problems are caused by the necessary requirement to define thermodynamically the initial and the final states of the evaporation process.

The description of gas flow in vacuum systems has been treated by Dushman and reference is made to his book for a detailed presentation[2]. The flow characteristics depend on the ratio of the mean free path of a molecule, L_a, to the radius of the orifice, a, through which the molecules pass. When $L_a/a > 1$ the flow is considered to be molecular and when it is $< 10^{-2}$ it is viscous. Between these limits the flow is in a transition range.

In the viscous flow region the flow is determined by collisions between gas molecules and the mass transport as given by Poiseuille's equation. In the molecular flow region collisions between the gas molecules and the walls of the system govern the mass flow, which can be described by Knudsen's equation. Between these extremes the flow characteristics vary continuously and no quantitative kinetic-theory analysis exists at the present time.

Considering the maximum weight of the evaporation chamber its size must be in the centimeter range. The size of the orifice is determined by the amount of substance necessary to vaporize under a reasonable length of time and it must lie in the range of a few tenths of a millimeter to a few millimeters. To estimate the mean free path of an organic vapor molecule at saturation pressure, we may chose the alkanes as models. The L_a-values can be obtained by the approximate equation[2]

$$L_a = \frac{2.331 \times 10^{-20}\ T}{p_{\mathrm{mm}}\ \delta^2}\ \mathrm{cm} \tag{1}$$

in which p_{mm} is the saturation pressure in mm Hg, T the temperature in °K and δ^2 stands as a measure of the collisional cross-section of the molecule. A very approximate value of δ^2 can be obtained from the constant b in van der Waal's equation and b can be calculated from the critical temperature and pressure of the substance by the relations

$$\delta^3 = 3b/2\pi N_A; \qquad b = R_o T_c/8P_c \tag{2—3}$$

in which N_A is Avogadro's number, R_0 the gas constant, T_c the critical temperature in °K, and P_c the critical pressure in atm. Hence

$$\delta^2 = 4.04 \times 10^{-16} \ (T_c/P_c)^{2/3} \text{ cm}^2 \tag{4}$$

From eqns. (4) and (1) together with data from Ref.[3] (vapor pressure, critical temperature and critical pressure) we obtain values for the mean free path of the even-numbered alkanes at saturation pressure and 25° (Table 1). Table 1 also gives vapor pressures at 25° and boiling points at 760 mm Hg.

Table 1.

n	8	10	12	14	16
b.p. (°C)	126	174	216	254	287
p (mm Hg)	14.0	1.37	0.13	0.0117	~0.001
L_a (cm)	0.00015	0.00135	0.012	0.12	1.3

Provided that saturation pressure prevails within the evaporation chamber, the flow characteristics then should be in the transition region in the pressure interval 1—0.01 mm Hg and change to molecular in the lowest pressure range 0.01—0.001 mm Hg.

The rate of evaporation. For the further analysis of the method chosen it is necessary to know the approximate rate of evaporation in the whole pressure range. In the molecular flow region the rate of evaporation is given by the Knudsen eqn. (5) which, provided certain conditions are fulfilled, simplifies to the Langmuir's formula (6) for evaporation from an open surface into empty space.

$$\frac{g}{t} = \frac{A_1}{1 + (A_1/A_2)} (p_1 - p_2) \sqrt{\frac{M}{2 \pi R_0 T}} \tag{5}$$

$$G = \frac{g}{A \cdot t} = p \cdot \sqrt{\frac{M}{2 \pi R_0 T}} \tag{6}$$

Here, g is the amount of substance (mol.wt. M) evaporating in time t through a hole of area A_1 out into a tube of area A_2 when the pressure in the evaporation chamber is p_1 and in the tube p_2. R_0 is the gas constant. If $A_1 \ll A_2$ and $p_2 \ll p_1$ eqn. (5) transforms into eqn. (6), in which G is the amount evaporated per unit time and unit area.

If $T = 298.16$°K, G is expressed in milligrams per minute and mm^2 and p in mm of Hg, eqn. (6) becomes

$$G = 2.027 \ p\sqrt{M} \tag{7}$$

We can now use this equation to obtain a rough estimate of the hole radius required to evaporate 10 mg of each of the hydrocarbons within 30 min. The results are found in Table 2 together with the corresponding G-values and ratios L_a/a. The rate of evaporation requirement, 10 mg in 30 min, represents a minimum and the L_a/a-values given are therefore maximum values.

It is seen that for $n = 8$ to 12 the flow is in the transition region, whereas from $n = 14$ it is molecular.

Table 2.

n	8	10	12	14	16
G	304	34	3.4	0.34	0.030
a (mm)	0.02	0.06	0.2	0.6	1.8
$L_a/a <$	0.08	0.25	0.6	2	7

For several reasons, however, the Langmuir and Knudsen equations should be of limited value in predicting rates of evaporation in the present case.

Firstly, these equations are applicable only in the molecular flow range — that is, in the lowest pressure region.

Secondly, the equations are valid only if the "length" of the orifice, s, is vanishingly small compared to its radius, a. The decrease in flow rate with increasing ratio s/a can be accounted for by introducing the Claussing factor [2], $K = f(s/a)$; $K \leq 1$. For $s = a$, which seems to represent a realistic value for the small holes with a diameter of a few tenths of a millimeter, K is 0.67, and the decrease is by no means severe. For $s = 0.3\,a$, which should be a reasonable value for the larger orifices, $K = 0.87$ — that is, the decrease in flow rate is only 13 %.

Thirdly, the Knudsen equation takes into account the influence of the residual pressure outside the evaporation cavity. If p_2 (eqn. 5) is of the same order of magnitude as p_1, the rate of evaporation decreases considerably. It is reasonable to assume that this factor may limit the use of the method in the low vapor-pressure range.

Knudsen's equation also shows the dependence of the rate of evaporation on the tube area A_2 outside the orifice area A_1 (eqn. 5). In a calorimetric experiment, it is always desirable to diminish the outside influence on the calorimeter proper by making all connections between the calorimeter and its surroundings as small as possible. This is in conflict with the requirement to increase the tube area outside the orifice in order to make A_1/A_2 small compared to 1 and also to decrease the pumping resistance, that is to decrease the residual pressure outside the evaporation chamber.

Finally, a condition which must be fulfilled if Knudsen's equation shall not be invalidated is, that the surface area of the vaporizing substance must be large compared to the orifice area. For larger holes this can be a critical condition.

In the transition flow range, the flow characteristics may vary from viscous to molecular. At the high pressure end the prevailing conditions are such that the vapor inside the evaporation chamber exhibits viscous properties, that the hole diameter is several times as large as the mean free path of the molecules and that — outside the hole — an adiabatic expansion takes place. This case has been theoretically treated by Nutt, Penmore and Biddlestone [5]. These authors derive the following equation for the ratio between the mass flow rate for frictionless adiabatic expansion, G_a, and the mass flow rate for molecular effusion, G_m:

$$\frac{G_a}{G_m} = D_c\left[2\,\pi\,\gamma\left(\frac{2}{\gamma+1}\right)^{(\gamma+1)/(\gamma-1)}\right]^{1/2} \tag{8}$$

Here γ is the ratio of the specific heats of the vapor and D_c a correction factor, usually between 0.5 and 1 and depending on the Reynold's number for the flow. For many organic substances the square root factor in eqn. (8) has an almost constant value. For octane through octadecane and propyl disulfide the average value is calculated to be 1.51 with a maximum deviation of 0.005. In practice, therefore, the flow rates in the higher pressure region do not deviate to any considerable extent from those calculated by the Langmuir equation.

As far as rates of evaporation are concerned it will therefore seem possible to build a calorimeter which fulfills the given requirements on size and weight and which still should be capable of allowing a sufficient amount of substance to be vaporized within a reasonable length of time.

Initial and final states of the vaporization process. It is an obvious requirement that the initial and final states of the vaporization process must be well known if the obtained ΔH_v-values shall be thermodynamically defined.

The initial state is the liquid at the calorimeter temperature and under the total pressure inside the evaporation chamber. The only unambiguity which should be considered is the surface temperature of the sample. The amount of evaporated substance is very small and at least for liquid samples the heat transfer can be made large enough to prevent the development of any significant temperature gradient within the evaporation chamber. It can be said, however, that for finely divided solids, this statement is not necessarily true, in which case precautions must be taken to ascertain a good heat transfer to the surface.

Unfortunately, the final state of evaporation is much more difficult — if not impossible — to define in a satisfactory way. To start with, the boundary of the calorimeter towards the pumping line is not sharp and it can be questioned where the calorimeter proper ends and the surrounding "jacket" begins.

It has been shown that the flow properties of the vapor change character almost completely within the pressure range of interest. Even for a system, which has been designed solely for the purpose of determining mass flow values, the problem of obtaining concordant results between experiments and theoretical predictions seems to be not an easy one, particularly not for fairly large non-spherical molecules. In the present work, the evaporation chamber must in the first place serve as a calorimeter and be of an appropriate construction. Therefore, the calculation of the flow characteristics and the estimation of the state in which the vapor molecules leave the calorimeter become even more complex.

As long as the vapor pressure inside the evaporation cup equals the saturation pressure, p_s, the heat of vaporization value obtained, ΔH_v°, of course refers to the evaporation at saturation pressure. If, however, the pressure inside the cup, p, is less than p_s, the vaporization occurs against $p < p_s$ and the isothermal work of expansion diminishes. In the limiting case, where the vaporization occurs against $p = 0$, the work is zero and the following relation holds:

$$\Delta H_v^\circ - \Delta H_v^{\text{obs}} = RT = 0.6 \text{ kcal.mole}^{-1} \text{ at } 25^\circ,$$

ΔH_v^{obs} being the observed heat of vaporization value.

The calculation of p now requires a knowledge of the flow properties and, as has been stated, these cannot easily be defined. It is therefore to be expected that systematic errors will show up in the experimental results — their magnitude and dependence on, *i.a.*, the saturation pressure can only be revealed by experiments performed on substances whose heat of vaporization values are well known.

It must also be considered that, from the point of view of irreversible thermodynamics, the effusion of an ideal gas represents not only a flux of mass but also a simultaneously occurring flux of energy (*i.a.* Prigogine[6]). In the case of effusion of an ideal gas the Onsager reciprocity relation and the Knudsen equation (5) lead to the surprising result, that the energy of the effused molecules is reduced by an amount of $1/2\ RT$ or about 300 cal.mole^{-1} at 25° as compared to the energy of the remaining molecules. In our experiments this "heat of transport" phenomenon represents a gain of heat for the calorimeter proper and the found heat of vaporization values will be 0.3 kcal.mole^{-1} too low. For pure diffusion processes, on the other hand, the heat of transport is zero and for the intermediate region no simple relationship exists [7].

It is also probable, that the flux properties of the residual gas will influence upon the results at least if the residual gas pressure is of the same order of magnitude as the vapor pressure of the substance itself.

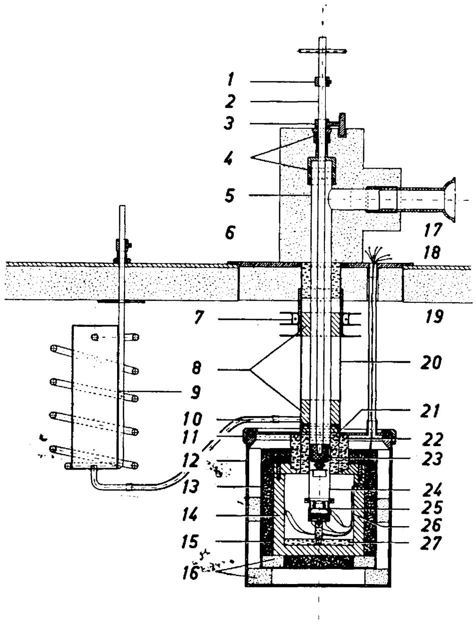

Fig. 1. Section through the assembled calorimeter set-up.

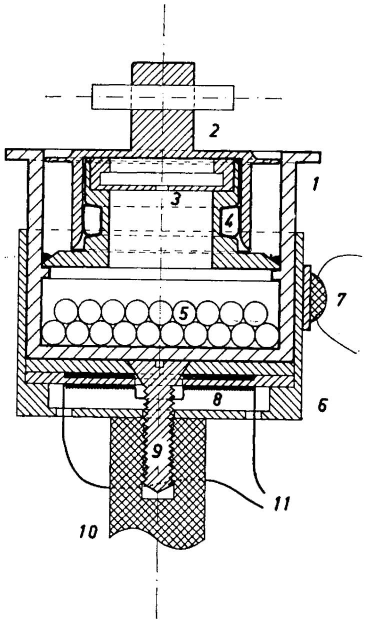

Fig. 2. Section through the calorimeter vessel: vaporization chamber and heating attachment.

INSTRUMENTATION

Calorimetric apparatus. The assembled apparatus is seen in cross-section in Fig. 1, and Fig. 2 shows the detailed design of the calorimeter proper.

The evaporation cup, 1, Fig. 2, is made of silver and carries an interchangeable disk, 3, with a central exit hole for the vapors. The chamber can be closed by the lid, 2, which is operated through a bayonet joint, the rubber O-ring, 4, gives a vacuum-tight seal. An increased thermal contact with the liquid sample is obtained by use of silver balls, 5.

The evaporation chamber fits precisely into a cup, 6, which carries the heater (leads, 11) and a thermistor, 7. The calorimeter proper — that is, evaporation chamber and cup, is supported on a lucite rod, 10, inside the surrounding cavity (Fig. 1). The air gap, 8, serves to prevent the direct heat transfer from the heater to the surroundings.

The surrounding calorimeter system (Fig. 2) consists of an outer brass can, 12, with lid and screw cap, 11. The lid has a central brass tube, 20, through which the evaporation cup is introduced and another tube for the leads to the thermistors, 25 and 26, and the heater. A second brass can, 13, is positioned centrally in the outer can using spacers of styro-foam, 16. In a similar way, a heavy-walled copper can, 14, is mounted inside 13 and constitutes the surroundings, as seen from the calorimeter proper. The space between 13 and 14 is filled with brass turnings.

The total system is submerged in a thermostat which keeps the temperature constant to within ± 0.001°C. To diminish the influence from outside variations, the lid, 18, of the thermostat carries a thick layer of surface-coated styro-foam and the tube, 20, is equipped with copper flanges, 7. The steel tube, 5 and 24, fits snuggly into the brass tube, 20, by use of the spacers, 21 (lucite) and 8 (copper). The vacuum line is attached by tube 17 via a ball-joint. The parts extending from the thermostat are insulated by styro-foam, 6.

The lid of the evaporation chamber is operated by the stainless steel rod, 2, which can be moved up and down and also turned round. The rod is centered in the head of the steel tube, 5; vacuum-tight seals are obtained by means of the O-rings, 4. The lower end of the rod is fastened to a teflon stopper inside a thin-walled steel cup which carries small spacers to achieve an accurate centering in the tube, 24, and also a bayonet joint (in Fig. 2 the lid of the evaporation chamber is hanging from the steel-cup). The stop-ring, 1, is adjusted so that the bayonet joint parts fit when the rod is in the lowest position and the stop-ring, 3, serves the purpose of fixing the rod when the lid is drawn up above the position of the joining evacuation tube, 17.

When the evaporation chamber is removed or inserted, air is sucked into or pressed out through the tube, 20, and the cavity within the copper block, 14. To avoid a direct exchange with the outside air, the inside space is connected by tube, 10, to an air reservoir, 9, which is in communication with the outside air through a spiral tube.

Vacuum-system. A high-vacuum was obtained by means of a two-stage oil diffusion pump with a liquid nitrogen trap together with a rotary oil fore-pump. A second liquid nitrogen trap was installed close to and thermally shielded from the evaporation chamber to freeze out the organic vapors. The pressure was measured by means of two Pirani gauges, one used for reading the fore-pump pressure, the second for the fine-pump pressure.

The air in the steel tube connected to the evaporation chamber could be pumped out or let in through a by-path without interrupting the finepressure pumping.

After 30 min. of pumping, a vacuum ot *ca.* 10^{-4} mm Hg was obtained. Depending on the vapor pressure of the substance the final pressure in the pumping line varied somewhat. Also, the slow contamination of the vacuum system by adsorbed vapors led to a decrease of the ultimate vacuum obtained.

Temperature measuring system. The temperature difference between the calorimeter proper and the surrounding copper block was measured by use of two thermistors (Stantel M 53, 5000 Ω at 20°) together with two 4000 Ω resistances in a conventional Wheatstone bridge curcuit. The thermistor in contact with the calorimeter had a lower resistance than the reference thermistor and the difference was compensated by use of a non-reactive decade resistance box (1111.11 Ω total resistance in 0.01 Ω steps).

The bridge was fed from a storage battery (2 V, 180 Ah), and the bridge current was adjusted to 250 μA. A Sullivan Type-M galvanometer (sensitivity 640 mm/μA) was used as zero-point instrument. The sensitivity was such that 1 mm scale deflection corresponded to 5×10^{-4} °C.

Electrical energy measuring system. The vaporization heat was electrically compensated by passing a known current through the calorimeter heater for a known length of time. The current through the heater was supplied from a storage battery (2 V, 180 Ah) which was under constant load during at least 90 min before the start of a series of experiments — that is, the current was passed through a dummy heater of the same resistance as the calorimeter heater.

In series with the heater were connected a non-reactive decade resistance box (totally 1111.11 Ω in steps of 0.01 Ω) and a standard resistance (5 or 10 Ω). The potential drop over the standard resistance was determined with a potentiometer, accurate to at least 2 parts in 10 000.

Time was measured with a stop-watch that could be started and stopped together with the heater current switch by a lever-mechanism. The time readings when the current was adjusted (see below) were taken down together with the potentiometer readings and the total amount of electrical energy supplied to the calorimeter was calculated from the readings and the known heater resistance, 61.402 Ω. The accuracy of the calculated total amount of electrical energy was estimated to be 0.1 % or better.

EXPERIMENTAL PROCEDURE

The evaporation cup was charged with *ca.* 300 mg of substance and a disk whose orifice was chosen to give a moderate evaporation rate was inserted. The lid of the evaporation cup was then fixed to the operating rod and the evaporation cup itself was attached to the steel tube by means of a screw cap. After thermal equilibrium had been roughly reached the tube was lowered into the thermostat system and connected to the vacuum line. The calorimeter was then slowly evacuated in order to avoid bumping — that is, loss of substance. The initial cooling effect inside the system by evaporation was electrically compensated. When a vacuum better than 10^{-3} mm Hg had been obtained, the evaporation was continued for a period of 10—20 min to eliminate small amounts of moisture which might be present and to determine the approximate heating current necessary for obtaining adiabatic conditions. Depending on the rate and heat of vaporization, the current varied between 5 and 15 mA.

The evaporation cup was then closed by lowering the operation rod and the heater current was switched off. By turning the rod through 90° it could be pulled away from the lid and air was let in. The vacuum-line was disconnected and the steel tube was pulled out. The evaporation cup was removed and weighed on a micro-balance. The cup was left on the balance for *ca.* 10 min and reweighed to disclose possible leaks. A further check on the tightness of the evaporation cup was then made by reweighing it after 15 min of pumping (vacuum better than 10^{-3} mm Hg, assembled system). If a change in weight of 10 μg or more was observed, the evaporation cup was considered to leak and usually a replacement of the O-ring was sufficient to give a leak-proof seal.

The cup was again attached to the steel tube, carefully cooled to a temperature slightly below 25° and inserted in a metal block in contact with the thermostat water. After equilibrium was reached (*ca.* 5 min) the calorimeter system was assembled and high-vacuum was produced. A slight cooling was unavoidable owing to the expansion of the air inside the steel tube and this effect was fully compensated electrically. When isothermal conditions had been established to within 0.00005°C (10 to 15 min.) the lid of the evaporation cup was removed and carried out of the vapor path to the top inside the steel tube. Simultaneously, the current was switched on and initially adjusted to a somewhat higher value than that which had been established during the fore-run. It was found that the opening of the cup invariably was accompanied by a small cooling effect, which probably was caused by an initial higher rate of evaporation before steady state conditions were reached in the space between the evaporation cup and the liquid nitrogen trap. This effect set in instantaneously; a maximum temperature drop of 0.003 to 0.005° was observed within 3 sec. After that the temperature increased as the supplied electrical energy was higher than the steady state heat of vaporization. The temperature was allowed to rise above that of the surroundings and it was possible to adjust the current so that a temperature-time curve resulted with almost equal areas below and above the zero-line. Thus, the gain and loss of heat caused by heat exchange with the surroundings nearly counterbalanced each other.

After 1—2 min isothermal conditions were established and could be kept to within ± 0.0002° with a few readjustments of the current (usually 5 in 30 min).

At the end of the measuring period, that is, after 10—30 min, the evaporation cup was closed, weighed and a subsequent experiment could be started immediately. With the same filling usually 5 to 8 experiments could be performed. After a series of measurements with one and the same substance the evaporation chamber and lid were thoroughly cleaned with benzene and acetone (ethanol) and then dried at *ca.* 130° in a stream of air. This procedure was repeated at least once to remove the last traces of sample.

TEST SUBSTANCES

One of the main obstacles to overcome in the present work was the lack of suitable reference substances for which heats of vaporization have been calorimetrically determined with an established accuracy. Although a great many vapor-pressure data are available in the literature, their reliability can very often be questioned. It was therefore felt desirable to use a series of compounds constituting part of a large assembly of homologous substances for which internally consistent thermodynamic data are available. Thus, it was obvious that hydrocarbons should be preferred [8] and a few of the alkanes were chosen as test substances.

As it should be of value to test the method also on some other substances, available samples of propyl disulfide and benzenethiol were investigated. Vapor pressure and heat of vaporization data for these compounds have been experimentally determined with high accuracy, although above room temperature. However, reliable extrapolated values of the heat of vaporization at 25°C have been published [9,10].

One way of testing the method would be to determine heat of vaporization and sublimation values for a substance that can be either solid or liquid at 25° and compare the difference with an independently determined value of the heat of fusion. This was done for phenyl diacetamide, which could easily be undercooled to 25° for 24 h.

Materials

Alkanes. Purum grade samples of *octane, decane, dodecane, tetradecane* and *hexadecane* were purified by fractional distillation and the purity was tested by GLC. It was estimated to be better than 99.5, 99.9, 99.0 and 99.8 % for octane, decane, dodecane and tetradecane, respectively. For unknown reasons the purity of hexadecane could not be established by GLC.

A 99.98 ± 0.02 mole-% pure sample of *hexadecane* was made available by the American Petroleum Institute through the API Research Project 44 at the A. and M. College of Texas. The sample was purified by the API Research Project 58 B at Carnegie Institute of Technology.

Samples of *propyl disulfide* and *benzenethiol,* of purities 99.9+ % as judged from GLC-analyses and iodometric titrations, were available.

A sample of *phenyl diacetamide,* m.p. 35, was obtained from Dr. Wadsö of this laboratory [11]. As judged from potentiometric titrations the purity was 100.0 %.

RESULTS

Results from representative series of measurements are summarized in Table 3. Column 1 gives the name and mol.wt. of the compound together with the approximate diameter of the orifice. Column 2 gives the evaporated amount in mg, column 3 the electrical energy in calories, supplied to the calorimeter, and the last column the computed heat of vaporization values.

Table 3.

Substance	mg	min	cal	ΔH_v kcal/mole
Octane	62.873	12.0	5.6213	10.21
M = 114.224	64.785	12.0	5.5422	9.77
Diam. 0.1 mm	45.548	8.5	3.8538	9.66
	60.953	10.0	5.1030	9.56
	60.654	10.0	5.0819	9.57
	42.934	7.5	3.7541	9.99
			Mean	9.79 ± 0.12
Decane	9.707	30.0	0.83878	12.29
M = 142.276	9.130	30.0	0.76965	11.99
Diam. 0.1 mm	8.766	30.0	0.72949	11.84
	7.695	30.0	0.64062	11.84
	8.244	30.0	0.68347	11.80
	7.755	30.0	0.67085	12.31
	7.722	30.0	0.64737	11.93
			Mean	12.00 ± 0.08
Diam. 0.2 mm	12.092	11.0	1.0177	11.97
	16.259	15.0	1.3599	11.90
	16.080	15.0	1.3766	12.18
	16.824	15.0	1.4201	12.01
	16.373	15.0	1.3822	12.01
	16.617	15.0	1.3976	11.98
			Mean	12.00 ± 0.04
Diam. 0.4 mm	38.836	10.0	3.2672	11.97
	46.165	12.0	3.9044	12.03
	38.972	10.0	3.2675	11.93
	46.626	12.0	3.9120	11.94
	50.587	13.0	4.2717	12.01
	46.670	12.0	3.9233	11.96
	50.483	13.0	4.2500	11.98
			Mean	11.97 ± 0.01
Dodecane	25.863	15.0	2.1845	14.39
M = 170.328	25.973	15.0	2.1813	14.30
Diam. 0.8 mm	25.722	15.0	2.1390	14.16
	25.780	15.0	2.1495	14.20
	25.882	15.0	2.1481	14.14
	26.043	15.0	2.1591	14.12
	26.080	15.0	2.1886	14.29
	26.024	15.0	2.1702	14.20
			Mean	14.22 ± 0.04
Tetradecane	5.553	20.0	0.46267	16.53
M = 198.380	5.608	20.0	0.46125	16.32
Diam. 1.0 mm	5.591	20.0	0.45864	16.27
	5.614	20.0	0.46429	16.40
	5.602	20.0	0.46625	16.51
	5.606	20.0	0.46741	16.54
			Mean	16.43 ± 0.05

Table 3, continued.

Substance	mg	min	cal	ΔH_v kcal/mole
Diam. 2.0 mm	22.961	20.0	1.8848	16.28
	11.425	10.0	0.9577	16.63
	20.700	18.0	1.7232	16.51
	20.805	18.0	1.7349	16.54
	20.808	18.0	1.7323	16.52
	20.900	18.0	1.7321	16.44
	14.450	13.0	1.2076	16.58
	14.517	13.0	1.1968	16.35
				Mean 16.48 ± 0.04
Diam. 3.1 mm	26.433	10.0	2.1825	16.38
	26.751	10.0	2.2175	16.44
	27.086	10.0	2.2451	16.44
	27.239	10.0	2.2501	16.39
	27.110	10.0	2.2477	16.45
	27.159	10.0	2.2388	16.35
				Mean 16.41 ± 0.02
Hexadecane	5.180	30.0	0.39061	17.07
M = 226.432	5.030	30.0	0.37194	16.74
Diam. 3.1 mm	5.113	30.0	0.37891	16.78
(without silver ball)	5.455	33.5	0.40225	16.70
	4.908	30.0	0.37094	17.13
				Mean 16.88 ± 0.09
Diam. 3.1 mm	21.015	52.0	1.5986	17.23
(with silver balls)	12.460	30.0	0.81755	14.86
	6.690	30.0	0.51542	17.44
	6.590	30.0	0.43406	14.91
	5.565	30.0	0.41221	16.77
Propyl disulfide	44.934	15.0	3.7820	12.65
M = 150.31	29.987	10.0	2.4908	12.49
Diam. 0.5 mm	45.012	15.0	3.7563	12.54
	30.504	10.0	2.5336	12.49
	30.342	10.0	2.5263	12.51
	30.165	10.0	2.5272	12.59
				Mean 12.55 ± 0.03
Benzenethiol	20.640	10.0	2.1356	11.40
M = 110.7	20.540	10.0	2.1145	11.34
Diam. 0.2 mm	20.419	10.0	2.0989	11.32
	20.448	10.0	2.1050	11.34
	20.503	10.0	2.1086	11.33
				Mean 11.35 ± 0.02

Table 3, continued.

Substance	mg	min	cal	ΔH_v kcal/mole
Phenyl diacetamide	11.300	40.5	1.3489	21.14
M = 177.10	5.486	20.0	0.63088	20.37
Diam. 3.1 mm	5.438	20.0	0.63615	20.72
(solid)	5.252	20.0	0.62116	20.95
(without silver balls)	5.550	20.0	0.65825	21.00
	4.970	20.0	0.58296	20.77
	5.396	20.0	0.62513	20.52
	5.218	21.0	0.60556	20.55
	8.545	30.0	1.0191	21.12
	8.759	30.0	1.0320	20.87
				Mean 20.80 ± 0.08
Diam. 3.1 mm	7.635	20.0	0.74135	17.20
(liquid)	7.783	20.0	0.74130	16.87
(without silver balls)	7.825	20.0	0.74504	16.86
	7.577	20.0	0.71047	16.61
	7.629	20.0	0.72353	16.80
	7.343	20.0	0.68638	16.56
	7.260	20.0	0.70234	17.13
				Mean 16.86 ± 0.08

After each series is given the average result of the measurements and its standard deviation; possible systematic errors have not been included.

The orifice diameters are given only approximately. Particularly the determinations of the smallest ones, 0.05 and 0.1 mm, are impaired by rather large errors.

Where not otherwise stated the experiments were performed with the silver balls in the evaporation chamber. In some cases the rate of evaporation decreased very much when the surface of the sample became partly shielded by the balls and satisfactory experiments could not be performed.

The heat of vaporization of phenyl diacetamide has not been reported in the literature. It was however possible to determine both the heat of sublimation of a solid sample as well as the heat of vaporization of a supercooled liquid sample at 25°. In the experiments with a crystalline sample, crystals were molten in the evaporation cup at 40° and cooled to room temperature. The liquid was seeded with a few crystals and the cup was set aside for 24 h at 0°. The supercooled sample was obtained by cooling the charged evaporation cup carefully from 40 to 25°. Between each run the cup was heated to 40° to diminish the risk for crystallization. The constancy of both rate and heat of vaporization between successive runs served as sensitive criteria for the absence of phase transisions.

The experiments with phenyl diacetamide were performed without the silver balls; in their presence the evaporation behaviour was irregular and the values obtained varied considerably. Besides, the balls frequently induced crystallization of the liquid sample.

DISCUSSION

It is first of interest to compare the experimentally determined rate of evaporation values with the values calculated from Langmuir's equation (Table 4, *cf*. Table 2).

The very close agreement is rather surprising considering the many factors that make the calculations very uncertain. However, it seems that Langmuir's equation can well be used for the approximate estimation of rates of vaporization even far outside the true molecular-flow range. A comparison between the L_a/a-values in Tables 2 and 4 also shows that the hole diameters were of about the same size as those estimated from the principal considerations.

A comparison between the average results for the n-alkanes and heat of vaporization data from the literature (Table 5) reveals the presence of a systematic error which increases with decreasing vapor pressure of the substance. The difference, $\delta\Delta H_v$, between the literature and the observed values can be expressed as the following linear function:

$$\delta\Delta H_v = \Delta H_v^0 - \Delta H_v^{obs} = 0.345 - 0.135 \log_{10} \frac{g}{td^2 \sqrt{M}} \tag{9}$$

where g is the amount in mg evaporated in t min. through a hole having a diameter of d mm. M is the mol.wt. and $\delta\Delta H_v$ is given in kcal.mole^{-1}.

From Table 5 it is apparent that the method completely fails for hexadecane. One reason for this could be that the residual pressure in the system has been close to the saturation pressure of the substance. That the residual pressure has a great influence upon the results obtained was made clear from a few preliminary experiments. When decane ($p = 1.4$ mm) was vaporized against fore-pump pressure, the heat of vaporization values obtained decreased from 11.7 kcal.mole^{-1} at *ca.* 10^{-1} mm to 9.5 kcal.mole^{-1} at *ca.* 1 mm. It is difficult to understand why the residual pressure has such a profound influence upon the heat of vaporization values. It could be that a recondensation occurs outside the evaporation chamber in the vicinity of the orifice and close enough to enable a transfer of part of the condensation heat back to the calorimeter. Only by specially designed experiments can a decision on this point be reached.

Although the logarithmic argument is proportional to pressure and in fact differs from Langmuir's equation only by a constant factor, we have preferred a form of the equation which contains only primary data. The closely linear relationship is apparent from Fig. 3, which also gives the uncertainties attached to the literature values of the heats of vaporization (vertical lines) as well as to the determined specific rates of evaporation (horizontal lines).

Table 4.

n	8	10	12	14	16
$G_{calc.}$	300	35	3.5	0.35	0.030
G_{found}	—	35	4	0.4	0.02
L_a/a	0.03	0.3−0.07	0.3	2.4−0.8	8

Table 5.

n	8	10	12	14	16
ΔH_v(lit.)	9.92 *	12.28 *	14.65	17.01	19.38
ΔH_v(obs.)	9.79	11.99	14.22	16.44	16.88

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* These values have been experimentally checked by Dr. I. Wadsö of this laboratory. He found the values 9.91 ± 0.03 and 12.25 ± 0.02 kcal.mole^{-1}, in excellent agreement with the API-values.

An examination of the data obtained for decane and tetradecane leads to two important conclusions. Firstly, the specific rate of evaporation, G, is approximately independent of the hole area, which is required both by the Langmuir equation and the equation of Nutt *et al.*[5], provided certain conditions, referring to the geometry of the hole, are fulfilled. In the experiments, described in the present report, no particular consideration was given to the relative geometry of the different orifices. For the larger apertures the length of the holes has varied between 0.3 and 0.5 mm and for the smaller holes between 0.2 and 0.4. The constant specific rate of evaporation for decane and tetradecane indicates that the variation in geometry of the holes had little or no significant influence upon the experiments.

Secondly, the heat of vaporization values obtained were found to be independent of the rates of evaporation at least within a ratio of 1 to *ca.* 15. This fact definitely proves that a significant temperature gradient caused by the heat transfer from the electrical heater to the surface of the sample does not build up during the experiment.

For propyl disulfide and benzenethiol the ΔH_v^0-values are 12.94 ± 0.10 and 11.64 ± 0.05 kcal.mole^{-1}, respectively. The results from the experiments show that eqn. (9) is also valid for these compounds, within the assigned uncertainties (Fig. 3). The error in the calculated correction, $\delta\Delta H_v$, is only 0.05 and 0.035 kcal.mole^{-1} for propyl disulfide and benzenethiol, respectively.

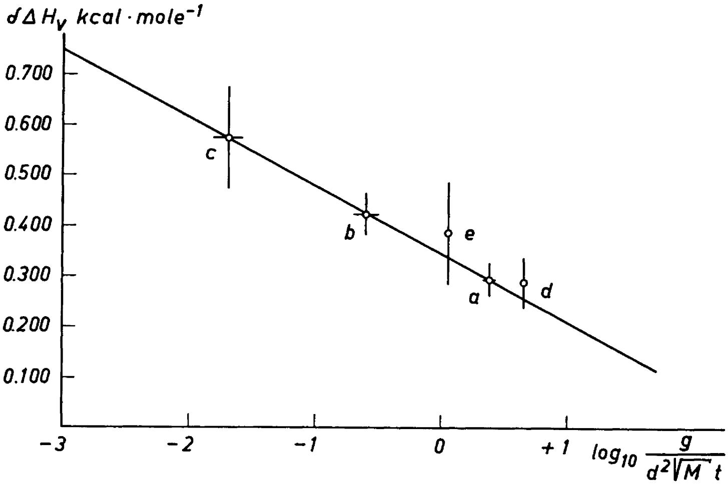

Fig. 3.

The experiments with phenyl diacetamide were mainly performed to find out if the correction derived for liquids could be applied also in the case of solids. If these corrections are applied, the heat of sublimation of solid phenyl diacetamide becomes 21.51 kcal.mole^{-1} and for the liquid sample 17.54 kcal.mole^{-1} is obtained. The difference between the ΔH_v-values is equal to the heat of fusion, which from the corrected values is found to be 3.97 ± 0.12 kcal.mole^{-1}. From heat of solution experiments the heat of fusion was calculated to be 3.88 ± 0.02 kcal.mole^{-1}. The difference between the two values is well within the assigned uncertainty. Thus, these experiments do not exclude the possibility that the correction is applicable also for solids.

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