

a platinum resistance thermometer to 0.001 K. At 550 K the failure to specify the scale introduces an uncertainty of 0.07 K. Platinum resistance thermometers have long lives if they are not broken, and many in use were calibrated by the manufacturer or at a standards laboratory on IPTS-48. There can be no objection to use of this scale provided it is declared, but on the other hand, there is little difficulty in applying the corrections detailed in Table I and changing the values to those on the current scale.

Thermodynamic arguments ought to depend on thermodynamic temperatures, but in most instances, experimental errors will cause greater uncertainty in any derived quantities than will arise from scale uncertainty. If, then, a sentence such as "Temperatures in this paper are expressed as International Practical Kelvin Temperatures T_{68} , which for most purposes are indistinguishable from the thermodynamic temperatures T ," or "which it is convenient to treat as interchangeable with thermodynamic temperatures T where no confusion arises and theoretical considerations do not demand differentiation of the two," is included in the text, it is quite clear what is being done and allows the author to write equations in terms of T , which is thermodynamically correct, rather than the cumbersome T_{68} . Sometimes, however, this approximation is inadequate and the author may need to maintain the distinction between T , T_{68} , and T_{48} . Here no problem arises as long as the author knows what he is doing and gets his subscripts in the correct places.

If the careful specification suggested is not given, a reader at some point will encounter difficulty. Corrections to the scale in future may be smaller than they were in the past, but

they will still be necessary and unless the numbers printed now are adequately specified, it may not be possible to apply them. There are papers of 30 years ago in which the authors have declared their temperatures are thermodynamic but do not say whether they added 273.15 or 273.16 to their Celsius temperatures, and it may not be obvious whether they have then adjusted their measured values by what were believed to be the true corrections. To unravel this difficulty, it is necessary to know the custom of the particular laboratory, and this may require extensive search through other papers which are not necessarily by the same authors. At the time, what was done no doubt seemed so obvious to the authors as not to need stating, but it is no longer obvious, and the same situation will arise in respect of papers written today if some things that seem self-evident are not recorded.

The objective of this article is action by authors in the future, not an account of the past—a history of temperature scales. The latter is complex, and simplification to make the presentation as brief as that just given, cannot fail to lead to minor errors in detail. For comprehensive and expert coverage of the subject, the reader is referred elsewhere (3–5).

Literature Cited

- (1) "The International Practical Temperature Scale of 1968," HMSO, London, England, 1969; *Metrologia*, **5**, 35 (1969).
- (2) Guildner, L. A., Edsinger, R. D., *J. Res. Nat. Bur. Stand.*, **77A**, 383 (1973).
- (3) Hall, J. A., *Brit. J. Appl. Phys.*, **1**, 81 (1950).
- (4) Hust, J. G., *Cryogenics*, **6**, 443 (1969).
- (5) Quinn, T. J., Compton, J. P., *Rep. Prog. Phys.*, **38**, 151 (1975).
- (6) Wexler, A., Greenspan, L., *J. Res. Nat. Bur. Stand.*, **75A**, 213 (1971).

Received for review August 7, 1975. Accepted December 24, 1975.

Determination of Saturated Vapor Pressure in Range 10^{-1} – 10^{-4} Torr by Effusion Method

Raúl S. DePablo

Diamond Shamrock Corp., P.O. Box 348, Painesville, Ohio 44077

An effusion method was used to determine the vapor pressure of six organic compounds, 3,3-dimethyl-1-(methylthio)-2-butanone *O*-[(methylamino)carbonyl]oxime, and *S*-ethylpropylpropynylcarbamothioate, one of its isomers, and three of its homologs at 25 and 40 °C. The vapor pressure of one novel organic compound, 3,3-dimethyl-1-(methylthio)-2-butanone *O*-[(methylamino)carbonyl]oxime, was determined at seven temperatures between 25 and 55 °C. The following equation was obtained from a computerized least-squares curve fit for its solid phase: $\log_{10} P = 15.34 \pm 0.98^* - 4882 \pm 305^*/T$, where P = vapor pressure, torr; T = absolute temperature; and * = confidence limits at 95% level. This equation can be used for calculating the vapor pressure at any desired temperature in the range of 25–55 °C.

The basic theory of the effusion method was reviewed in the literature (2, 3, 5, 12). The apparatus used consisted of the following basic parts: a large tube for the effusion cells placed in a constant temperature bath, a cold trap (dry ice and acetone), a pressure gauge, and an oil diffusion pump backed by a mechanical pump. Temperature was controlled

to ± 0.05 °C by a mercury-glass thermoregulator in conjunction with an electronic relay. The temperature of the bath was read from ASTM certified thermometers provided with correction charts and considered to be equal to the temperature of the samples. After the organic compounds were prepared, they were purified by recrystallization from chloroform–hexane or vacuum distillation at about 0.004 torr and 60–65 °C. Structure and chemical names of the compounds used in this investigation are listed in Table I.

Effusion cells were made of stainless steel, with threaded lid, a stainless steel foil with the effusion hole, and a Teflon washer. Since the cells were calibrated with pure mercury whose vapor pressure was taken as a standard, there was no need to know the effusion hole area, thickness, and correction factors. In each determination, two calibrated effusion cells were placed in the large tube for the cells. Under these conditions, the operation was greatly simplified and accelerated.

Safety. All compounds cited in Table I should be handled wearing gloves and a respirator.

The cells were calibrated by placing pure mercury in each cell, tightening the lids with a wrench, weighing to ± 0.1 mg, and introducing the cells into the apparatus and evacuating quickly to a pressure about 0.1 or less of the vapor pressure to be determined. After a suitable time, the vacuum was bro-

ken, and the cells were removed and reweighed. These data were used in the following equation to calculate the effusion cell constant:

$$K = \frac{Pt}{\Delta} \sqrt{M/T} \quad (1)$$

where K = effusion cell constant; P = vapor pressure of mercury, torr, at temperature T (taken from tables); T = absolute temperature of bath; Δ = decrease in weight of cell, g; t = effusion time, s; and M = atomic weight of mercury or molecular weight of the compound in the gas phase. Once the constant K is known, this same value is used to calculate any unknown vapor pressure by rearranging Equation 1 to Equation 2:

$$P = \frac{K\Delta}{t} \sqrt{T/M} \quad (2)$$

Results and Discussion

Equation 2 requires a knowledge of the molecular weight of the compound in the gas phase. Table II presents the constants of cells 1 and 2, when both were present in the apparatus as determined by the above procedure.

For each cell, the value finally taken was the average of the above values ($K_1 = 7013$, $K_2 = 8458$). This final value for the constant was used to calculate the unknown vapor pressures at all temperatures. Effusion hole diameters were 0.60 and 0.54 mm for cells 1 and 2, respectively. There seems to be some small variation of the cell constant with the effusion time.

This procedure was checked against mercury and several known organic compounds. Our values for mercury at 90 °C for 10 determinations showed an average of 0.162 torr and a standard deviation of 0.008 torr. These results show the average is 3% higher than the literature value of 0.158 torr (17) and has a precision of $\pm 5\%$. The effusion hole diameters were, as before, 0.60 and 0.54 mm.

Table III shows our values of vapor pressure for organic compounds compared with literature values. There seems to

Table II. Effusion Cell Constants^a

Approx effusion time, h	Cell constants, torr·s·g ⁻¹ ·deg K ^{-0.5}					
	Cell 1			Cell 2		
	<i>n</i> ^b	Av	SD ^c	<i>n</i>	Av	SD
24	11	6889	107	11	8387	58
48	7	7012	212	7	8533	98
72	5	7028	129	5	8484	143
96	4	7123	361	4	8427	167

^a Bath temperature = 25.00 \pm 0.05 °C. ^b *n* = number of determinations. ^c SD = standard deviation.

Table III. Vapor Pressure of Organic Compounds^a

Compound	Vapor press, m torr				
	This work			Lit	Ref
	Av	<i>n</i>	SD		
<i>p</i> -Chloronitrobenzene	23.3	2	...	21.8	(9)
<i>p</i> -Chloroaniline	23.8	7	0.4	27.7	(9)
Benzoic acid	0.81	2	...	0.76, 0.65	(6)
Benzoic acid (45 °C)	7.73	6	0.09	6.34	(6)
(70.5 °C)	89.4	5	8.97	92.6	(1)
				73.3 (extrapolated)	(6)
Benzophenone (55.9 °C)	23.6	4	3.48	20.1	(12)
(60.7 °C)	32.1	2	...	30.0	(12)
(66.9 °C)	54.6	2	...	50.0 (extrapolated)	(12)
(71.2 °C)	71.5	6	4.70	70.0 (extrapolated)	(12)
Salicylic acid (70.5 °C)	21.4	6	1.99	25.2 (extrapolated)	(1)
<i>o</i> -Anisic acid (80.0 °C)	20.2	4	2.09	27.2	(1)
Naphthalene	101.2	18	4.2	100.3	(4)
				82.0	(8)
Trifluralin ^b (30 °C)	0.197	3	0.015	0.2	(7)
Eptam ^c	39.8	6	1.5	35 (extrapolated)	(13)
Temik ^d	0.06	1	...	0.10	(10)
Temik (50 °C)	0.9	1	...	0.7	(10)

^a Temperature 25.00 \pm 0.05 °C, except as noted. ^b *N,N*-Diethyl-2,6-dinitro-4-(trifluoromethyl)benzenamine. ^c *S*-Ethylpropylcarbamothioate. ^d 2-Methyl-2-(methylthio)propanol *O*-{(methylamino)carbonyl} oxime.

be good agreement between our values and those of the literature, except perhaps in the case of naphthalene. If the value 82.0 m torr is taken as exact, our high results might be explained for some volatile impurity present in the naphthalene used, which was Fisher certified, without further purification.

Effusion hole diameters used ranged from 0.6 to 0.1 mm. The higher the pressure, the lower the diameter used. The ratio between the mean free path of the molecules inside the cells and the diameter of the effusion hole ranged from 43 (benzoic acid at 45 °C) to 1.7 (naphthalene at 25 °C). Ratios for the last three compounds were not calculated for lack of other data, but presumably they were above 40. Mean free paths were calculated as an approximation by the equation of kinetic theory (2).

The following equation, based on the data of Table IV, was obtained from a computerized least-squares curve fit for the solid phase (melting range 57–58 °C).

$$\log_{10} P = 15.34 \pm 0.98 - \frac{4882 \pm 305}{T}$$

Table I. Name and Structure of Compounds

Compound	Name	Structure
A	3,3-Dimethyl-1-(methylthio)-2-butanone <i>O</i> -{(methylamino)carbonyl} oxime	
B	<i>S</i> -Ethylpropylpropynylcarbamothioate	
C	<i>S</i> -Ethyl(isopropyl)propynylcarbamothioate	
D	<i>S</i> -Ethyl(2-methylpropyl)propynylcarbamothioate	
E	<i>S</i> -Ethylbutylpropynylcarbamothioate	
F	<i>S</i> -Propynylidipropylcarbamothioate	

where P = vapor pressure, torr; T = absolute temperature; and \pm = confidence limits at 95% level. These equations can be used for calculating the vapor pressure at any desired temperature in the range 25–55 °C.

Differential scanning calorimetry did not detect any phase change below the melting point. Tests were run to check the thermal stability of compound A. This was heated in a Pyrex glass ampule, under a nitrogen blanket ($P < 0.02$ torr), for about 110 h at a fixed temperature. The ampule was cooled to room temperature, broken, and compound A analyzed by liquid chromatography for the presence of extraneous peaks. The test at 51 °C showed no extraneous peaks, but tests at 70 and 85 °C did show an extraneous small peak indicating decomposition. These tests show that vapor pressures determined above the melting point are not reliable due to thermal decomposition and, for this reason, are not included here.

Results shown in Table IV were obtained with the following range of parameters: effusion hole diameters, 0.54 and 0.60 mm; mean free path to hole diameter ratio, approximately 190:8; effusion times, 70–190 h; weight variation of the cells, 0.007–0.0990 g; and thickness of effusion foil, about 0.03 mm.

In some cases, vaporization occurred preferentially near the walls, since a small void was observed after the run between the walls and the sample. We think that a difference of temperature between the sample and the bath, if any, should be negligible at these low pressures.

The vapor pressure of five other organic compounds determined at two temperatures are shown in Table V.

As already established in the theory, the requirement is that the diameter of the effusion hole shall be about 10% or less of the mean free path of the molecules inside the cell. However, good results can still be obtained when the diameter is about the same as the mean free path. A series of effusion foils with holes of different sizes, all calibrated, will allow the determination of vapor pressure over a wide range. Since the cells and the pressure gauge indicating the pressure outside the cells are generally at different temperatures, a correction should be applied to the reading. In our case, this correction was negligible.

Acknowledgment

The author thanks C. L. Sieglaff for construction of the vacuum system and C. J. Kingery for making the effusion cells.

Table IV. Vapor Pressure of Compound A

Temp, °C	Vapor press, m torr		
	<i>n</i>	Av	SD
25.00	4	0.094	0.02
30.00	2	0.19	...
35.45	2	0.30	...
40.00	2	0.525	...
45.00	2	0.995	...
50.00	2	1.72	...
55.00	2	3.05	...

Table V. Vapor Pressure of Organic Compounds, m torr

Com- pound ^a	25.00 °C			40.00 °C		
	Av	<i>n</i>	SD	Av	<i>n</i>	SD
B	17.70	1	...	61.7	2	...
C	16.00	2	...	65.3	1	...
D	10.96	3	0.38	45.8	2	...
E	5.00	2	...	24.45	2	...
F	2.95	2	...	17.60	2	...

^a See Table I for name and structure.

Literature Cited

- (1) Davies, M., Jones, J. I., *Trans. Faraday Soc.*, **50**, 1042 (1954).
- (2) Dushman, S., "Scientific Foundations of the Vacuum Technique", 2nd ed., pp 30, 38, 90, Wiley, New York, N.Y., 1962.
- (3) Hollahan, J. R., *J. Chem. Educ.*, **39** (1), 23 (1962).
- (4) Hughes, E. E., Lias, S. G., NBS Technical Note No. 70, National Bureau of Standards, Washington, D.C., 1960.
- (5) Knudsen, M., *Ann. Phys.*, **28**, 75, 999 (1909); **29**, 179 (1909).
- (6) McEachern, D. M., Sandoval, O., *J. Phys. Sci. Instrum.*, **6**, 155 (1973).
- (7) Rose, H. A., Eli Lilly Co., Indianapolis, Ind., private communication, 1971.
- (8) Sinke, G. C., *J. Chem. Thermodyn.*, **6**, 311 (1974).
- (9) Swan, T. H., Mack, Jr., E., *J. Am. Chem. Soc.*, **47**, 2112 (1925).
- (10) Union Carbide Corp., Bulletin Aldicarb 10-G, 1970.
- (11) Weast, R. C., Ed., "Handbook of Chemistry and Physics", p D-150, Chemical Rubber Co., Cleveland, Ohio, 1972.
- (12) Weissberger, A., "Techniques of Organic Chemistry", Vol 1, Pt. 1, 3rd ed., pp 462, 464, Interscience, New York, N.Y., 1959.
- (13) Zweig, G., "Analytical Methods for Pesticides, Plant Growth Regulators, and Food Additives", Vol IV, p 118, Academic Press, New York, N.Y., 1964.

Received for review February 18, 1975. Accepted November 8, 1975.