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63-3-5

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404 919

16 May 1963

RSIC-13

THE EVAPORATION OF SOLID BODIES

By

M. K. Baranov

From

Zhurnal Fizicheskoi Khimii, Akademiya Nauk, SSSR
20, 399-402 (1946)

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THE EVAPORATION OF SOLID BODIES

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M. K. Baranaev

Up until now, kinetics of evaporation of solid bodies were studied in much less detail than kinetics of evaporation of liquids. However, in certain instances which present an interest from the practical viewpoint, it becomes necessary to solve problems related to the kinetics of evaporation of solid bodies. In particular, when clarifying the laws of evaporation, it is very convenient to use solid liquid drop models, the sizes of which may vary as desired.

However, it must be stated here that evaporation of solid bodies follows the same law as evaporation of liquids, or at least, conditions under which such a state is valid must be precisely determined.

Mack /1/ used the rate of evaporation of solid iodine in stationary air when making determination of the diffusion coefficient of iodine vapors. He presumed that evaporation occurs in such a manner, that directly over the iodine surface there is a layer of a saturated vapor, and that the rate of evaporation is determined by the rate of vapor diffusion in the surrounding medium, i.e., the same process occurs as during evaporation of liquids.

Langmuir acted likewise when calculating the diffusion coefficient of iodine on the basis of data obtained by Morse/2/ for evaporation of iodine bubbles. Topley and Whytlow-Gray/3/ repeated Morse's and Mack's tests and performed a calculation analogous to that of Langmuir. The values of the diffusion coefficients obtained by Topley and Whytlow-Gray, based on Mack's and Morse-Langmuir methods, concurred well with each other.

This concurrence indicates that evaporation of solid bodies in stationary air apparently occurs in the same way as the evaporation of liquids, i.e., above the surface of an evaporating body a layer of saturated vapor actually exists; if the same is valid, also, during rapid evaporation in moving air, then all obtained formulas for evaporation of liquids are applicable for calculating evaporation rate of solid bodies; and vice versa, the laws of evaporation of liquid bodies (drops) may be studied by measuring the rate of evaporation of solid models. In order to correctly solve this problem, it is required to know the rate of evaporation of a solid body in a vacuum. Assumption on the existence of a saturated vapor layer is valid only in the instance when the rate of evaporation in a vacuum is considerably greater than the rate of evaporation in air. The rate of evaporation in a vacuum may be calculated by Knudsen's formula; during this, however, it is essential to know the values of coefficients of accommodation.

We performed measurements of accommodation coefficients for ice, solid phenol, solid benzene and camphor. The results are given below.

METHODS OF DETERMINATION

To determine the coefficients of accommodation we used a device similar to the one used by Alty /9/ in his measurements. A schematic drawing of the device is shown in Fig. 1. The end of pipe A was submerged into the melted substance under investigation (retort B was removed during this time). Pipe A was cooled during the tests with ice and benzene by mercury, and by running water during tests with iodine, phenol and camphor.

A layer of solid substance with a sufficiently smooth surface frosted

on the end of pipe A. The surface of the pipe end was considered to be spherical. The value of the surface layer of the evaporating substance was calculated by the height and radius of the spherical segment, which was measured by means of a cathetometer.

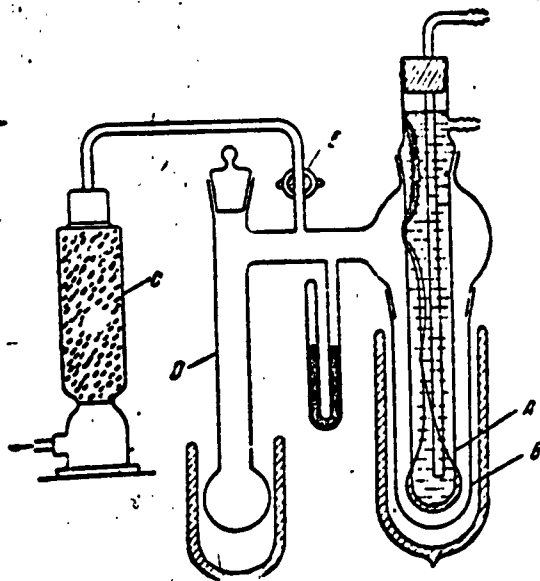


Fig. 1

For measuring temperature in the layer of the investigated substance, a copper-constantan thermocouple junction was frozen to the end of pipe A. The other thermocouple junction was placed in the thermostat either at 0°C (in ice) or at $38,9^{\circ}\text{C}$ (in mercury).

Pipe A (after measurement of the surface layer of the substance at its end) was sealed off by retort B. Air was pumped out of the device by an oil-pump. A certain amount of the substance was heated in pipe D for the

purpose of expelling any remaining air from the device. To avoid condensation, the same temperature as that of pipe D was maintained during this period along the walls of retort B. Vapors forced the air out and were absorbed by activated carbon in column C. After a period of 10 - 15 minutes, cock E was closed, and pipe D was cooled by liquefied nitrogen.* During this the vapors filling the device condensed in pipe D, resulting in the evaporation of the substance from the surface of pipe A. After a few minutes when a proper vacuum was established, retort B was also submerged into a Dewar flask containing liquefied nitrogen, and all substances evaporating at this time from the end of pipe A condensed on its walls. The absence of the migration of molecules from retort B to pipe D during intense cooling of both flasks can be easily explained by the fact that condensation of the substance evaporating from the end of pipe A was no longer noticed on the upper sections of retort B. Ten to fifteen minutes after start of condensation in retort B air was admitted into the device, retort B was removed, closed with a stopper and weighed.

Following this, the substance was washed off the interior walls of the retort with a solvent, which was introduced into and removed from the retort by means of a pipet so as not to affect the lubricant on the slide of the retort. Then the retort was dried by a stream of warm air and weighed again (together with the stopper). The quantity of the substance condensed on the walls of retort B (or the quantity of the substance evaporated from the end of pipe A) was determined by differences in weight.

The accommodation coefficient α was calculated by Knudsen's formula /4/

* In tests with iodine and camphor, a cooling mixture of dry ice with acetone was used instead of liquefied nitrogen.

$$\alpha = \frac{w}{P} \sqrt{\frac{2\pi RT}{M}}$$

Here w is the rate of evaporation in $\frac{\text{g}}{\text{cm}^2 \text{ sec}}$, R is the gas constant in $\frac{\text{ergs}}{\text{g-molecule}}$, P is the vapor pressure in bars, M is the mass of a gram-molecule in grams. Test data is given in Table I.

Table I

Substance	Evaporation surface S	Temp surface of evaporat. T _v (vapor)	Press. of saturated vap. P _v in mm Hg.	Evaporation Time t, sec	Quantity of evap. subst. Q in g	Evaporation rate $w = \frac{Q}{S \cdot t}$	Accommodation coefficient α	Average value of α
Benzene	11.4	220	0.22	300	1.5672	$3.4 \cdot 10^{-4}$	0.61	0.62
	15.6	213	0.11	300	0.5811	$1.46 \cdot 10^{-4}$	0.51	
	15.0	221	0.24	300	1.7900	$3.98 \cdot 10^{-4}$	0.71	
Ice	16.6	225	0.018	300	0.1811	$3.7 \cdot 10^{-6}$	0.059	0.066
	16.6	223	0.051	300	0.3598	$7.2 \cdot 10^{-6}$	0.071	
	15.0	227	0.058	300	0.3660	$8.1 \cdot 10^{-6}$	0.073	
Iodine	8.0	281.3	0.067	300	0.8152	$3.4 \cdot 10^{-4}$	0.95	0.96
	8.0	276.9	0.043	300	0.5570	$2.3 \cdot 10^{-4}$	0.93	
Camphor	6.07	278.5	0.053	300	0.0700	$3.9 \cdot 10^{-6}$	0.17	0.17
	12.83	277.4	0.050	300	0.1382	$3.6 \cdot 10^{-6}$	0.17	
	6.8	285.2	0.096	300	0.1521	$7.5 \cdot 10^{-6}$	0.16	

Table II

Substance	Accomd. coeff. α	Literature Source	Substance	Accomd. coeff. α	Literature Source
Solid Bodies			Liquids		
Th. Ts. W	1.0	[7]	CCl ₄	1.0	[9]
Cl	0.98	[6]	H ₂ O	0.01	[9]
Hg	0.85	[5]	CH ₃ OH	0.01	
J	0.91	Table 1 [9]	C ₂ H ₅ OH	0.02	
C ₁₂ H ₂₂ O	1.0	[9]	C ₄ H ₉ OH	0.02	Kinetics of evaporation Progress in Chemistry No. 8, 1938 by Baranaev
C ₁₀ H ₁₆ O	0.29	[9]	CHCl ₃	0.17	
C ₁₁ H ₁₆	0.62	Table 1	C ₆ H ₆	0.23	
H ₂ O (ice)	0.018	[9]	C ₁₂ H ₂₂ O	0.17	
C ₁₀ H ₁₆ O (camphor)	0.17	Table 1 [9]	C ₁₁ H ₁₆	0.16	

By comparing the values of α obtained by various testers (see Table II), it may be easily seen that the accommodation coefficients of solid bodies have the same order as the accommodation coefficients of liquids; therefore, the rates of evaporation in a vacuum and in air for both liquefied and solid bodies are approximately the same.

Thus, the evaporation of solid and liquefied bodies in air conforms to the same law.

I express my gratitude to I. A. Mirkin for his series of valuable comments.

Submitted *
12. 11. 1946

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* Initial data was submitted to Editor on 20 May 1940.