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TRANSLATION

VAPOR PRESSURE AND EVAPORATION OF SUBSTANCES IN MOVABLE AIR

By

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FOREIGN TECHNOLOGY
DIVISION

AIR FORCE SYSTEMS COMMAND

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by

V. G. Matsak

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The purpose of this report was to provide hygienists and engineers, working in the field of sanitation technology, with concrete and founded data on vapor pressure and rate of evaporation in movable air of various inorganic and organic substances.

Special attention was devoted to substances, most frequently used in technology, and to toxic substances as well. The knowledge of these data will allow hygienists to evaluate the potential danger during evaporation of toxic substances in relation to their phys-chem. and toxicological properties, and will allow sanitation engineers to use same for making calculations of air exchange, quantitative determination of the degree of weighting air during the evaporation of substances with greater molecular weight, proper distribution over the influx and expansion zones and other measures of improving labor conditions at industries.

Vapor pressure of each substance ordinarily can be expressed in a considerable temperature interval in form of logarithmic equation:

$$\log P_n = -\frac{A}{T} + B \qquad (1)$$

Here P_n - pressure of saturated vapor of a substance in mm Hg at absolute temperature T; A and B are constants, characteristic for each substance. In text books for a majority of substances are given numerical values of these constants.

Determination of vapor pressures by equation (1) is connected with the necessity of fatiguing searcher for data in text books and with the possibility of errors during calculations. That is why it is proposed for technical and sanitation-technical calculations, where a 5% error is of no considerable importance, to employ nomograms. One of these nomograms (fig. 1) was introduced by prof. V. A. Kireyev. In this nomogram as standard substances were accepted hexane and water. This nomogram was expanded by the author with 16 new substances added to it. Here were not included aromatic nitro-and amino compounds, for which the author has compiled a second nomogram; here are given also certain other substances, having an analogous law of change in pressure of saturated vapor with the change in temperature (fig. 2). The third nomogram (fig. 3) was compiled by the author for vapor pressure of certain molten metals and salts. As a standard in the last two nomograms were accepted nitrobenzene and lead.

As an example of employing nomograms we will assume, that it is necessary to know the pressure of saturated vapor of carbon tetrachloride at a temperature of 20°. In the list of substances, appended to fig. 1, carbon tetrachloride is marked under number 14a. We place the ruler so that it will pass through point 14a and point, corresponding to a temperature of 20°. The intersection of ruler with vertical line of vapor pressure shows, that the vapor pressure of carbon tetrachloride at 20° equals about 90 mm Hg.

If it is necessary to establish the boiling point of methylamine, marked under number 28, we place the ruler so that it runs through 760 mm and point 28. We find that the boiling point of methylamine equals - 4°.

The pressure of saturated lead vapor at 500° according to nomogram (fig. 3) constitutes about 0.00001 mm Hg. This corresponds to a concentration of 0.0043 mg/m^3. But in compartments, where the work with molten lead is carried out, is often observed a considerably higher concentration. This can be explained by the fact, that lead vapor condenses, converts into dust particles of very minute dimensionality, which settle slowly. The concentration of lead aerosol will depend upon the rate of deposition and may become much higher than the concentration of lead vapor at the moment of evaporation.

It should be pointed out, that certain lead compound, e.g. lead sulfide and lead chloride, as is evident from nomogram No. 3, are much more volatile, than metallic lead. When remelting scrap lead, coming from chemical plants, this circumstance may considerably increase the concentration of lead compounds in the air. The presently employed method of sampling lead in the air by absorption of nitric acid allows to determine the entire lead content in the air, regardless of the fact, in what form it was - in metallic or in form of chemical compound.

Knowing the maximum vapor pressure of the substance under ordinary meteorological conditions, it is possible to determine the corresponding to it concentration in the air. For this purpose it is necessary to use equations introduced by the author together with prof. L. K. Khotsyanov in 1944:

$$C = \frac{P_n M}{18.3} \qquad (2)$$

Here C - concentration (mg/l), M-molecular weight of substance, P_n-pressure of saturated vapor of substance at 10-20° and normal atmospheric pressure.

We will assume, that the pressure of acetic anhydride vapor, saturated at 20°, according to nomogram No. 2 equals 2.7 mm Hg. It is necessary to determine the maximum possible concentration of same in the air. Substituting in equation (2) $P_n = 2.7$ and $M = 92$, we will obtain, that maximum possible concentration of acetic anhydride at 20° equals 15.5 mg/l.

If it is necessary to determine, what concentrations may form in a cistern used for carrying benzene after it has been drained at a 10° temperature of outside air, it is necessary to use formula (2).

Ordinarily a cistern is not emptied completely during the decantation. A certain amount of the liquid remains on the bottom, especially in the presence of rust and sludge.

Consequently in "empty" cisterns and volumes the air can attain total saturation by the vapor of a substance, which was situated in it before. As result of benzene evaporation the temperature of the air in the cistern drops at first, and then on account of heat transfer through the walls it rises to the temperature of outside air.

By nomogram 1 we find that the pressure of saturated benzene vapor at 10° equals 40 mm Hg. The molecular weight of the benzene equals 78. To obtain a corresponding concentration we will substitute the numerical value in equation (2).

$$C = \frac{P_n \cdot M}{18.3} \quad \frac{40 \cdot 78}{18.3} = 170 \text{ mg/l}$$

This concentration of benzene is above maximum permissible with respect to H 101-54 by 3400 times. It is also higher than the lower limit of explosion (48.7 mg/l).

It is known, that the rate of water evaporation and the evaporation of other substances is proportional to the pressure differential of saturated vapor of the pressure in the air, surrounding the substance. For a majority of instances the parctically characteristic difference of evaporation of anhydrous substances in movable air and evaporation of water is this, that evaporation of substances takes place in the air, containing no vapor of the substance or containing amounts of same very far from saturation. For example, if evaporation of benzene takes place in the air, containing 1 mg/l of benzene, which exceeds by twenty times the maximum permissible concentration, then this high concentration constitutes at 20° only 0.3% of the total saturation.

The temperature of substances during evaporation in moving air decreases depending upon their volatility. Such easily volatile substances, as ether, carbon disulfide, may reduce their temperature by tens of degrees. The problem concerning the degree of temperature reduction of substances is not sufficiently elucidated in literature. Well investigated was the reducing temperature of evaporating water, approaching in a sufficiently mobile air the temperature of a humid thermometer. In 1938 we derived an equation to determine the temperature of evaporating water, and in 1951 - an equation to determine surface temperature of any evaporating substances in moving air. To evaporate substances in moving air containing no vapor of the substance or containing insignificantly small amounts of same, this equation has the following form

$$0{,}24\,t_c = 0{,}24\,t_{\text{вл}} + (L + C_{\text{п}} \cdot t_{\text{вл}}) \frac{34{,}5\,P_{\text{н}} \cdot M}{(B - P_{\text{н}})\,1000} \qquad (3)$$

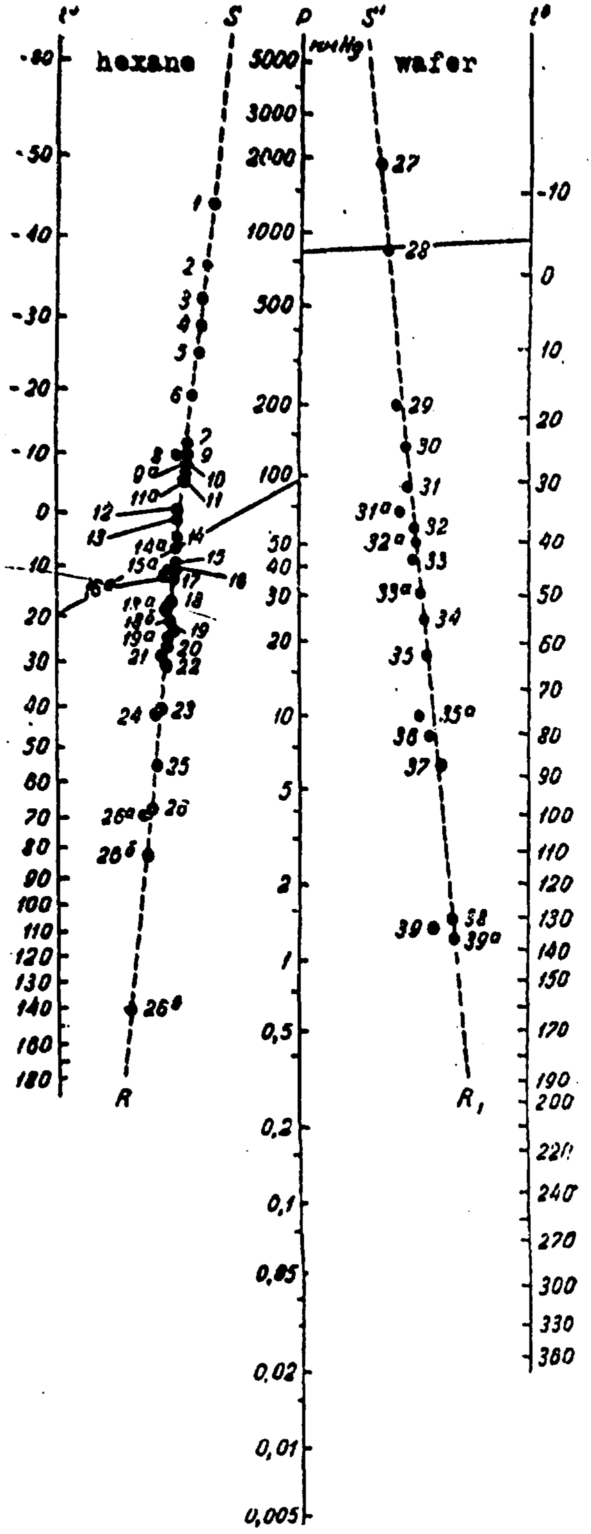

Fig. 1. Nomogram of saturated vapor pressure for chemically pure substances (according to V. A. Kireyev and data by the author); 1-methylsilican; 2-propadiene; 3-methyl chloride; 4-vinyl chloride; 5-butadiene; 6-ethyl chloride; 7-isoprene; 8-methylformiate; 9-centane; 9a-diethyl ether; 10-ethyl bromide; 11-chloromethylene; 11a-carbon bisulfide; 12-ethylformiate; 13-chloroform; 14-n-hexane; 14a-carbon tetrachloride; 15-benzene; 15a-trichloroethylene; 16-ethylacetate; 16a-dichloroethane; 17-fluorobenzene; 18-n-heptane; 18a-ethylpropionate; 18b-propylacetate; 19-toluene; 19a-tetrachloroethylene; 20-n-octane (w); 21-n-octane (l); 22-chlorobenzene; 23-bromobenzene; 24-n-decane; 25-iodobenzene; 26-naphtalin; 26a-camphor; 26b-diphenyl; 26c-anthracene; 27-ammonia; 28-methylamine; 29-acetone; 30-methyl alcohol; 31-ethyl alcohol; 31a-formic acid; 32-water; 32a-propyl alcohol; 33-acetic acid; 33a-butanol; 34-propionic acid; 35-isobutyric acid; 35a-valeric acid; 36-n-butylene thiocol; 37-ethyleneglycol; 38-glycerin; 39-mercury; 39a-mercuric chloride.

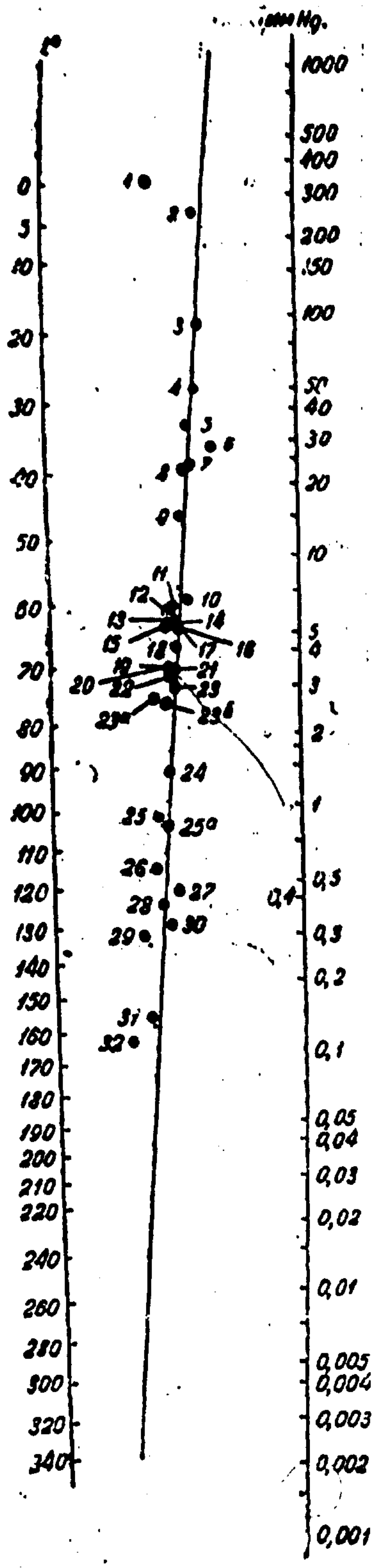

Fig. 2. Nomogram of saturated vapor pressure of chemically pure substances (according to the author), 1-nitric tetroxide; 2-isopentane; 3-phosphorus trichloride; 4-nitromethane; 5-chloropicrin; 6-sulfur monochloride; 7-tetranitromethane; 8-arsenic trichloride; 9-acetic anhydride; 10-dimethylaniline; 11-aniline; 12-phenol; 13-benzoyl chloride; 14-o-toluidine; 15-methylaniline; 16-n-toluidine; 17-ethylainline; 18-nitrobenzene; 19-o-nitrobenzene; 20-diethylaniline; 21-antimony trichloride; 22-m-nitrotouene; 23-n-nitrotouene; 23a-dimethylparatoluidine; 23b-quinoline; 24-phthalic anhydride; 25-o-nitrotoluene; 25a-diphenyl; 26-nitroglycerin; 27-arsenous acid anhydride; 28-dibenzylketone; 29-n-nitroaniline; 30-trinitrotoluene; 31-mercurous chloride; 32-anthraquinone.

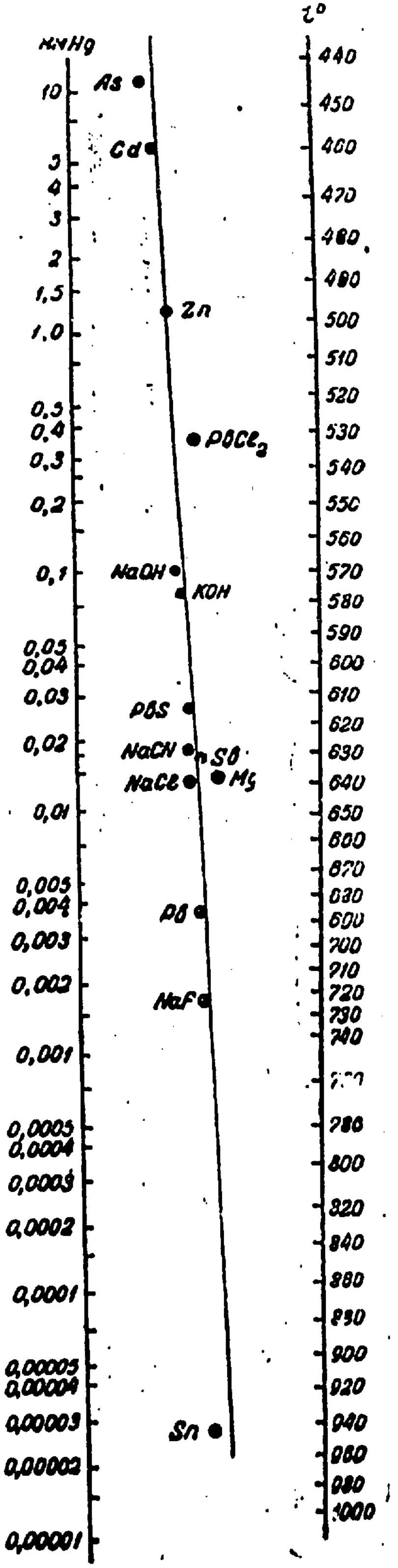

Fig. 3. Nomogram of saturated vapor pressure of chemically pure substances (according to the author).

where t_c - temperature of air, moving at a certain distance along the surface of the evaporating substance; t_{vl} - temperature, to which the surface of the evaporating substance tends; L-latent temperature of substance evaporation at 0° (in kcal/kg); C_p-specific heat at constant vapor pressure of the substance (in kcal/kg); ; P_n-pressure of saturated vapor of substance at t_{vl} (in mm Hg); B -atmospheric pressure (in mm Hg).

By this equation were calculated temperatures, to which the surfaces of various substances do tend during evaporation in moving air. An experiment was made, by wetting the bead of the moisture thermometer of the aspiration psychrometer with various substances, as for example, with alcohol, chlorobenzene, aniline, having different boiling point. Experimental and calculation data are compiled in table 1.

Table 1. Temperature of substances during evaporation in movable air

Substance	B.p. at pressure of 760 ...	Temper. of air.	Temp. of evapor. subs.		Vapor pressure at evapor. temp. of substance (in mm Hg).
			calcul.	exper.	
Mercury	360°	20°	19,997°	--	0.0012
Diphenyl	255°	20°	19.95°	—	0.03
Naphtalin	218°	20°	19.6°	19.6°	0.05
Nitrobenzene	210.8°	20°	19.1°	19.1°	0.22
Aniline	184°	20°	18.8°	18.9°	0.3
Chlorobenzene	132°	20°	12°	13°	6
Amyl alcohol	137.7°	20°	14°	15°	2
Benzene	80°	20°	-5°	0°	17
Ethyl alcohol	78.7°	20°	2°	5°	11.6
Dichloroethame	83.7°	20°	-2°	1°	16
Acetone	56.1°	20°	-17°	—	28
Ethyl ether	34.6°	20°	-28°	--	43

Examining table 1 it will be noticed: a) for substances boiling at above 250°, the temperature drop during evaporation in movable air at normal atmospheric pressure is insignificant; b) for substances, boiling at temperatures of from 184° (aniline) to 218° (naphthalin) the temperature drop is 1,2° to 0.4°; c) for substances, boiling at 132-137.7° temperature drop is 6-8°, d) for substances, boiling at about 80°, temperature drop in dry air may reach 20-25°.

It should be mentioned, that a reduction in temperature for low boiling substances may come close to calculated under conditions, if the air is sufficiently dry. During humid air the temperature drop cannot be much lower than the dew point. Moisture condensing on the surface of the substance, gives up its latent heat to the substance and interferes with the temperature reduction of the substance. During the experiments the temperature drop was somewhat lower, than by calculations, but very close to calculated.

The rate of evaporation was mostly investigated for water. Among the greater number of equations for the rate of water evaporation in moving air data closest to experimental are furnished by calculation in accordance with equation, introduced by the All Union Heat technical Inst.

$$S = (22{,}9 + 17{,}4\,V)\,(P_n - P_1) \qquad (4)$$

where S - weight rate of evaporation (in g/m^2 hr); V-rate of motion of the air (in m/sec); (P_n--P_1- pressure differential of saturated vapor at a temperature of evaporising water and water vapor, contained in the air, moving above the water.

The process of evaporation of other substances differs from water evaporation by the following:

a) vapor density of substances differs from water vapor and is proportional to the molecular weight. And so, vapor density of benzene at identical pressures is greater than that of water vapor by 78:18 = 4.3 times, where 78 - molecular weight of benzene, and 18-molecular weight of water;

b) evaporation of substances usually takes place in the air, containing none of its vapor or containing same in quantities, very far from the limit of saturation. And so, benzene at a concentration of 1 mg/l at 20° saturates space only by 0.3%. Under such conditions the two-member P_n-P_1 in its absolute value approached P_n - pressure of sa substance vapor at the temperature of its evaporation.

We made the assumption, that the rates of evaporation of water and other substances are similar to the outflow of vapor through openings at small pressure differential.

The linear rate of outflow equals:

$$\Omega = \sqrt{\frac{2g \cdot \Delta P}{\gamma}} \qquad (5)$$

where omega - rate of outflow (in m/sec); g-acceleration of gravitation force, equaling 9.8 m/sec^2; Δp - pressure differential (in kg/m^2); gamma-weight of 1 m^3 of vapor (in kg).

From equations (5) and (4) was derived the following equation for the rates of evaporation of substances in movable air:

$$S = (5{,}38 + 4{,}1\,V)\,P_{H}\sqrt{M} \qquad (6)$$

where M - molecular weight of substance. Remaining designations and dimensions the same as in equation (4). To check the correctness of this equation we made an experiment to determine the rate of toluene evaporation (boiling point 104°), chlorobenzene (132°), aniline (184°), naphthalin (218°) and water in the air, moving over the surfaces of these substances at speeds of from 0.25 to 5 m/sec.

Measurement results are given in table 2.

Examining table 2 one can notice greater conformity in calculated and experimental data, which allows to propose for the determination of weight rate of substance evaporation in the air the previously mentioned equation (6).

The temperature of the evaporized substance can be calculated by equation (3) or take same in analogy with any other substance, listed in table 1.

Pressure of saturated vapor at a temperature of evaporised substance can be determined with the aid of introduced nomograms. And so, if it is necessary to determine the rate of evaporation of spilled nitrobenzene from an area with a surface of 2 m^2

at an air temperature of 20°, at an air mobility of 3 m/sec, in the absence of radiant heat then according to table 1 we find, that the temperature of the evaporating surface wil equal 19.1°.

Table 2. Calculated and experimental rate of evaporation in moving air

Date	Substance	Rate of air motion m/s	Surface of evapor cm^2	Air temperat.	Temp of wetted surface	Amount of evapor.substance		Differ betw exp. & cal	Remark
						exp.	calc		
6.22.54	Toluene	5	12	22°	7°	3,01	2,98	+1	Air desiccated in exper.
		3	12	22°	7°	1,94	2,03	—4,5	
		1	12	22°	7,1°	1,16	1,09	+6,4	
		0,5	12	22°	7,3°	0,78	0,86	—10	
5-18 20	Chlorobenzene	5	12	17,2°	13°	1,92	1,95	—1,5	
		3	12	17,2°	13°	1,4	1,34	+4,5	
		1	12	17,2°	13,2°	0,775	0,725	+6,9	
		0,5	12	17,2°	13,4°	0,6	0,56	+7,1	
5-27 6-8	Analine	5	8	17,2°	16°	0,06	0,061	—1,6	Data of second ser.of invest.
		3	8	17,2°	16°	0,041	0,038	+8	
		1	8	17,2°	16,2°	0,018	0,02	—10	
		0,5	8	17,2°	16,2°	0,014	0,015	—6,7	
		0,25	8	17,2°	16,2°	0,014	0,013	+6,7	
6-1-17	Naphthalin	5	24,6	17,3°	17°	0,03	0,03	0	
		5	24,6	17,3°	17°	0,031	0,03	+3	by loss in weight
		3	24,6	17,3°	17°	0,021	0,022	—5	by analys
		3	24,6	17,3°	17°	0,023	0,022	+5	by weight loss
		1	24,6	17,3°	17°	0,011	0,011	0	analycis
		1	24,6	17,3°	17°	0,01	0,011	—10	weight loss
		0,5	24,6	17,3°	17°	0,01	0,009	+10	analysis wght loss
6-25	Water	5	12	22	11	0,75	0,76	—1,30	

Pressure of nitrobenzene vapor at 19.1° according to nomogram No. 2 equals 0.22 mm Hg. Molecular weight of nitrobenzene equals 123. Substituting the numerical value in equation (6), we will obtain:

$$S = (5.38 + 4.1\ V)\ P_n \sqrt{M} = (5.38 + 4.1 \cdot 3)\ 0.22 \sqrt{123} = 43\ g/m^2\ hr$$

The amount of evaporizing nitrobenzene from a 2 m^2 surface equals 86 g/hr. This small amount may contaminate a considerable volume of air. According to H 101-54 the maximum permissible concentration of nitrobenzene is 0.005 mg/l (g/m^3). Nitrobenzene vapor in the amount of 86 g/hr may produce this concentration in a ventilated volume $\frac{86}{0.005} = 17200\ m^3/hr.$

Summary

The author has worked out a nomogram for determination of elasticity of of saturated vapour and a method of calculating the rate of evaporation of various chemical substances in moving air. These data are necessary for evaluation of potential danger of toxic substances and for calculation of industrial ventilation.

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