Letters

Saturation Vapor Pressures over Supercooled Water

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In analyses of certain nucleation problems in cloud physics, estimates of the saturation vapor pressure over water at very large degrees of supercooling are needed. For example, since nucleation of a liquid phase from a supersaturated vapor phase is thermodynamically more probable than nucleation of a solid phase from the same vapor, prediction of nucleation rates in clouds at very low temperatures calls for such information on saturation vapor pressures over highly supercooled water. Formation of nacreous clouds [*Hesstvedt,* 1960] provides a particular instance of that type, and homogeneous nucleation processes in rapid adiabatic expansions constitute another case of theoretical interest. Since the degree of ice-supersaturation of a vapor saturated with respect to liquid water is an important parameter in the theory of ice nucleation [*Fletcher,* 1962] the same data are of interest in that connection also.

Tabulations of the saturation vapor pressure e_w over supercooled water are presented in the *Smithsonian Meteorological Tables* [*List,* 1951] only down to $-50°C$. Those tabulations are based on the Goff-Gratch formulation, a thermodynamically consistent extrapolation beyond the limit of direct experimental determinations of e_w. Although further extrapolation of the Goff-Gratch relation to temperatures still lower than $-50°C$ clearly involves uncertainty, nevertheless that relation provides the best basis for estimates of low-temperature values of e_w presently available. For this reason, it is probable that other investigators seeking one or more values of e_w below $-50°C$ will do as I have recently had to do, namely, compute estimates based on the Goff-Gratch equation.

The Goff-Gratch equation in the form given by *List* [1951] contains some typographical errors. *Goff* [1957] has presented a revision of this equation, including proper allowance for the 1954 international redefinitions of the Kelvin temperature scale and of the triple point of water. Subsequently some further slight revisions in certain of the numerical coefficients of the 1957 formulation have been made by Goff (kindly communicated to me by L. P. Harrison), bringing it into the following form:

$$\begin{aligned}\log_{10} e_w(\text{mb}) &= 5.02800 \cdot \log_{10} (T_1/T) \\ &- 10.795737(T_1/T - 1) \\ &+ 1.50475 \times 10^{-4}[1 - 10^{(8.2969(1-T/T_1))}] \\ &- 0.42873 \times 10^{-3}[1 - 10^{-(4.76955(T_1/T-1))}] \\ &+ 0.7861406 \end{aligned} \qquad (1)$$

where $T_1 = 273.16$ is the triple point of water in degrees Kelvin, and $T = 273.15 + t$, t being the temperature in degrees Celsius.

Because of the tediousness of computing even a few values of e_w from (1) when they are needed in particular studies, it seemed desirable to use an automatic computer to systematically extend the evaluation of (1) down to the lowest temperatures likely to be of interest in any cloud physics estimates of nucleation rates. In Table 1 are presented values of e_w for each integral degree Celsius from $-50°C$ to $-100°C$. They are given to three digits, but it is unlikely that more than the first two are significant [see *List,* 1951, p. 350]. The value for $-50°C$ differs by about 1% from that given in *List* [1951], this difference resulting from the slight revisions in the Goff-Gratch relation since 1951.

I have also computed the ratio e_w/e_i, where e_i is the saturation vapor pressure over ice, using the Goff-Gratch e_i values given by List in the full range $0°C$ to $-100°C$, along with

TABLE 1. Values of e_w in the Range -50°C to -100°C, Computed from Equation 1

T, °C	e_w, mb	T, °C	e_w, mb
−50	6.47×10^{-2}	−76	2.21
−51	5.78	−77	1.91
−52	5.15	−78	1.64
−53	4.58	−79	1.41
−54	4.07	−80	1.21
−55	3.62	−81	1.03
−56	3.21	−82	8.82×10^{-4}
−57	2.84	−83	7.52
−58	2.52	−84	6.40
−59	2.22	−85	5.44
−60	1.96	−86	4.61
−61	1.73	−87	3.90
−62	1.52	−88	3.30
−63	1.34	−89	2.78
−64	1.18	−90	2.34
−65	1.03	−91	1.97
−66	9.03×10^{-3}	−92	1.65
−67	7.90	−93	1.38
−68	6.90	−94	1.15
−69	6.02	−95	9.58×10^{-5}
−70	5.24	−96	7.96
−71	4.55	−97	6.60
−72	3.95	−98	5.46
−73	3.43	−99	4.51
−74	2.97	−100	3.71
−75	2.56		

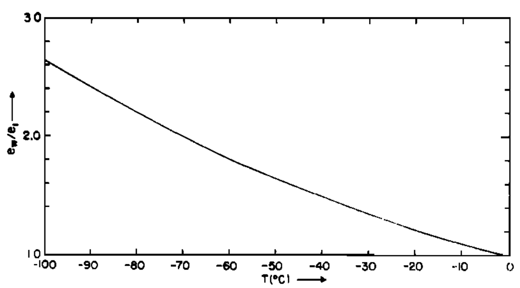

Fig. 1. Ratio of saturation vapor pressure over supercooled water e_w to saturation vapor pressure over ice e_i from 0°C to −100°C, based on Goff-Gratch formulation.

List's e_w values for 0°C to -50°C and the present extrapolations of e_w to -100°C. The results are displayed in Figure 1 for the information of investigators needing them for ice-nucleation calculations.

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