EFFECTS OF SURFACE PROPERTIES OF THE CONDENSATE ON THE CONDENSATION COEFFICIENTS OF ALKALI METALS

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It is shown that the condensation coefficients for alkali metals can differ appreciably from unity if impurities are present.

The condensation coefficient f defines the proportion of incident vapor molecules that will actually condense on the surface: this is governed by the activation energy at the vapor–condensate interface (Fig. 1) [1].

We derive f as the probability of passage of a molecule through a potential barrier of height ε via statistical mechanics [2], which gives

$$f \approx \exp\left(-\frac{\varepsilon}{kT}\right). \tag{1}$$

This f tends to determine the condensation rate; it is itself determined by the surface state of the condensate and the interaction of the condensing molecules with the surface.

It is often difficult to calculate f because we lack evidence on the surface structure and the nature of the interaction.

The f for water is very dependent on surface properties; water is highly polar, and the molecules are oriented at the surface. Nonequilibrium states can arise during orientation; the surface tension increases and so does f [1]. It has been found repeatedly that surfactant films retard the evaporation of water; they reduce the surface tension perhaps to 28 dyne/cm [3] and reduce f by 10-60%. Some adsorption layers (e.g., a monolayer of a 0.01% of hexanol) may increase the evaporation rate, however.

Liquid alkali metals belong to the class of simple liquids; the molecules are nonpolar and spherically symmetrical, and one does not expect any special surface properties. However, the metals react vigorously with oxygen and attack their containers, taking up other elements to form alloys. Alkali metals also often contain impurities; for example, Na usually contains K, etc. These impurities affect the surface structure and energy.

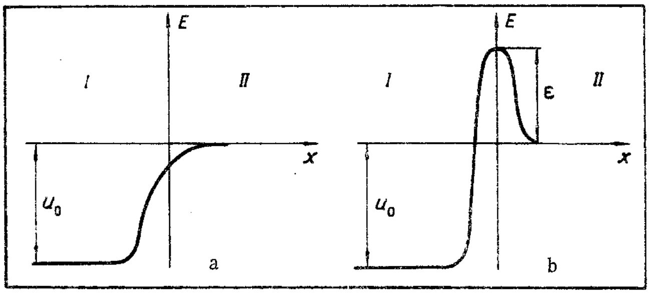

Fig. 1. Physical model for the determination of the condensation coefficient: a) activation energy at $\varepsilon = 0$; b) activation energy at $\varepsilon \neq 0$; I) condensate; II) vapor.

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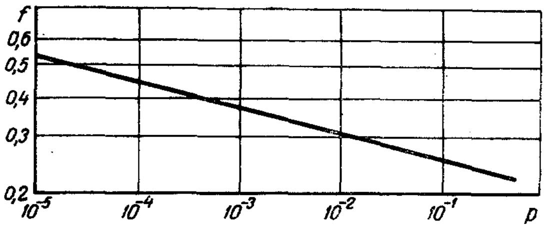

Fig.2. Condensation coefficient of sodium containing 0.034 wt.% oxygen as a function of pressure (mm Hg).

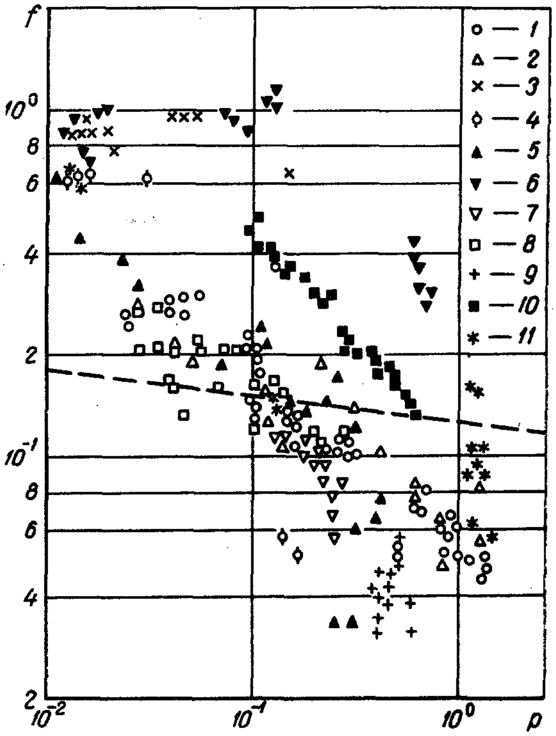

Fig.3. Comparison of experimental data and the results of calculations: 1-5) K; 6-9) Na; 10, 11) Rb; 1) [8]; 2, 8) [10]; 3) [11]; 4) [12]; 5) [13]; 6) [14]; 7) [18]; 9) [15]; 10) [16]; 11) [17].

It has been shown [5] that the surface tension of sodium at 260°C can be reduced by about a factor 2 by 0.034 wt.% oxygen, while 50% potassium in sodium (at 250°C) reduces the surface tension by a factor of 1.5 or so. The surface tension may be expected to influence f.

The mechanical state of any inhomogeneous system is defined by specifying the pressure tensor P for each point in the system. For a planar layer of finite thickness τ, the mechanical work of deformation δW is determined by P_N, the normal component of the pressure tensor, which is constant in this system, and by the surface tension σ [6]:

$$\delta W = -P_N\delta V + \delta A \int_0^\tau (P_N - P_T)\,dz = -P_N\delta V + \sigma\delta A. \tag{2}$$

Work $\sigma\delta A$ is then done on passing through the surface; if σ alters, this work is changed by $\Delta\sigma\delta A$, and we can say that the latter is the potential barrier at the vapor – condensate interface, and f for this case can be calculated from (1) with

$$\varepsilon = \Delta\sigma S. \tag{3}$$

We have $S = \delta A$ in (3), this being the area taken up by one molecule on the surface of the condensate, which is defined as follows [7]:

$$S = \left(\frac{M}{N\gamma}\right)^{2/3}. \tag{4}$$

We have $\Delta\sigma = 0$ and f = 1 if the condensate contains no impurities, but f can differ appreciably from 1 if $\Delta\sigma \neq 0$.

Figure 2 shows f for sodium containing 0.034% oxygen, as calculated from surface tension data [5]; f decreases as the pressure increases, as is usual for condensing vapors [8].

It is usually found [9] that f does not differ substantially from unity in condensation tests at low temperatures, because the impurity content in the condenser is much lower than that in the boiler.

Figure 3 compares the f reported for pressures of 10^{-2} to 10^0 bar; the broken line shows f as a function of pressure as derived by extrapolating the results of Fig.2. The values calculated from (1) for 0.034 wt.% oxygen in the condensate fall in the range of f reported by various workers. It should be borne in mind that this oxygen content is close to the level at which the experiments might be done.

The comparison between experiment and theory in Fig.3 is very crude, since it is necessary to know the impurity content of the metal in the condenser in each particular case.

The results from (1) and (3), together with tests, show that f = 1 is to be expected for a pure alkali metal, but that f may differ considerably from 1 if there are impurities.

To determine f in any particular case it is necessary to know the exact impurity content of the liquid metal in the condenser; in addition, data on the effect of impurities and temperature on the surface tension are necessary.

NOTATION

f is the coefficient of condensation;
ε is the height of the potential barrier (activation energy for condensation);

k is Boltzmann's constant;
T is the temperature of the vapor;
W is the mechanical work of deformation;
V is the volume;
A is the area of the surface discontinuity;
P is the pressure tensor;
P_N is the normal component of the pressure tensor;
P_T is the tangential component of the pressure tensor;
σ is the surface tension;
S is the area occupied by one molecule on the condensate surface;
M is the molecular weight;
N is Avogadro's number;
γ is the specific weight;
p is the vapor pressure.

LITERATURE CITED

1. N.N. Kochurova, Trudy TSKTI, Kotloturbostroenie, Issue 12, Leningrad (1969).
2. L.D. Landau and E. M. Lifshits, Statistical Physics [in Russian], Fizmatgiz, Moscow (1959).
3. M. Baranaev, Zh. Fiz. Khim., 13, 1635 (1939); 9, 69 (1937).
4. B. V. Deryagin, S. P. Bakanov, and Yu. S. Kurgin, Dokl. Akad. Nauk SSSR, 135, 1417 (1960).
5. D. H. Bradhurst and A. S. Buchanan, Australian J. Chem., 14, No. 3, 397 (1961).
6. A.I. Rusanov, Phase Equilibria and Surface Phenomena [in Russian], Khimiya (1967).
7. Ya.I. Frenkel', Collected Works [in Russian], Vol. 3, Izd. AN SSSR, Moscow–Leningrad (1959).
8. I.T. Aladyev, N.S. Kondratyev, et al., Film Condensation of Sodium and Potassium Vapor, 3rd Int. Heat Transfer Conf. Chicago, Illinois, 11 (1966), p.313.
9. V.I. Subbotin, M.N. Ivanovskii, V.P. Sorokin, and B.A. Chulkov, Teplofiz. Vys. Temp., No.4 (1964).
10. D.A. Labuntsov and S. I. Smirnov, Proceedings of Third International Heat Transfer Conference, Chicago, Illinois, 11 (1966), p.329.
11. S. F. Wilcox and W. M. Rohsenow, Rep. No. DSR, 71475-62, Dep. of Mech. Eng., MIT (1969).
12. M. L. Morin, P. M. Meyrial, and W. M. Rohsenow, Report No. 70008-52. Eng. Projects Lab. MIT, Cambridge, Mass. (March 1968).
13. D. G. Kroger, Thesis (Sc.D), MIT, Cambridge, Mass. (1966).
14. V. I. Subbotin, N.V. Bakulin, M.N. Ivanovskii, and V.P. Sorokin, Teplofiz. Vys. Temp., No.5 (1967).
15. R. E. Balzhiser, R.L. Gaham, and A. J. Sartor, Technical Report AFAPLTR, 66-85 (1967).
16. A.J. Sartor, R. E. Balzhiser, and R. E. Barry, Report on 11 National Heat Transfer Conference, AIChE-ASME, Minneapolis, Minnesota, August 1966.
17. C. R. Fisher and J.R. Moskowitz, AGN-8162 (January 1966).
18. R.E. Barry, Doctor's Dissertation, The University of Michigan (1965).