EFFECT OF GAS ON SURFACE TENSION OF POTASSIUM

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The surface tension of a liquid drop has been studied by many authors, but the results of their studies differ significantly. Even if we exclude from consideration the data of [1], [2], and [3] because of serious procedural errors and metal contamination, the remaining data of [4-8] and the data of [9], obtained by withdrawing a vertical plate, differ from one another by an amount which exceeds considerably the overall measurement errors. It is true that all the studies other than [4] found similar values of the surface-tension temperature coefficient. All the measurements encompassing larger or smaller temperature ranges were performed in inert gas atmospheres of different purity and it is possible that this is the reason for the discrepancies.

To clarify this question we must carry out studies over a quite wide temperature range in both a gaseous atmosphere and in the atmosphere of the saturated vapors themselves. None of the existing methods permit carrying out these studies at temperatures up to 1300° K and saturated vapor pressures reaching several atmospheres.

There is a combined method which permits measurement of the surface tension of aggressive liquids at high pressures and high temperatures in both the atmosphere of the vapors themselves and the atmosphere of an inert gas. The results of a study using this method of the surface tension of certain liquids are presented in [9] and [10].

The studies described here were made on the experimental setup shown in Fig. 1.

The two fine working capillaries 1 with internal diameter 0.09 cm were inserted into the 0.2-cm-diam. tubes 2. The sleeve 3 with these tubes was placed in the thinwalled cylinder 4. The tubes were joined by common chambers at the top and bottom. The cylinder 4 communicates with the third glass capillary 8 through the intermediate separating vessel 9 which serves for filling the system with the test metal. The cylinder with the capillary is placed in the nickel thermostating block 5, heated by a controllable electric heater with a system of screens. To prevent pressure loads on the cylinder it is placed under a cooled metal hood in which the pressure is held close to the working pressure in the cylinder. The upper chamber of the cylinder communicates with the capillaries 4 and the glass tube 8 through a large vessel 13, which makes it possible to vary the pressure in the system smoothly. The temperature of the test section was measured by two platinum–platinum-rhodium thermocouples. The accuracy of the temperature measurement could be checked by the saturation pressure, which was also measured in each experiment.

Prior to beginning the experiments the entire system was baked to 400° C (and the cylinder with capillaries to 700° C) and evacuated to $\sim 10^{-5}$ mm Hg. Then the potassium at a temperature of 70° C was introduced from the sylphon type portioning device 10 into the cylinder with the capillaries through the intermediate vessel 9. For better wetting the intermediate vessel with the metal was heated for 3-5 h at 400° C. After heating the metal cooled. The cold metal in the intermediate vessel was covered from the reservoir 7 through the tube 8 with degassed transformer oil which served as the intermediate liquid. After establishing a definite oil level in the glass tube 8, the cylinder 4 with capillaries was heated to a specified temperature. In this process the vapor phase of the test metal appears in the upper chamber of the cylinder. If the gas pressure in the tube 8 becomes somewhat less than the saturated vapor pressure in the upper chamber of the cylinder 4, the metal will be displaced from the cylinder by its own vapor and the oil level in the glass tube 8 correspondingly begins to rise slowly. Upon transition of the metal from the capillaries 1 into the tubes 2 two discontinuities of the oil level are observed in the glass tube

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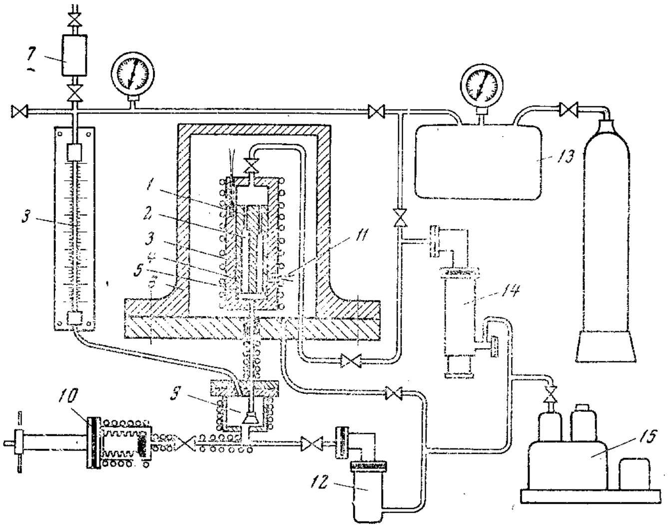

Fig. 1. Schematic of experimental setup for measuring surface tension of potassium.

8. By measuring the distance between the two discontinuities in the tube 8 we can determine the potassium surface tension from the formula

$$\frac{\sigma}{\rho' - \rho''} = C_1 h_3 - C_2$$

Here σ is the surface tension, ρ' and ρ'' are the densities of the liquid and vapor phases, h_3 is the distance between the discontinuities in the tube 8, and C_1 and C_2 are instrument constants, which depend only on the system geometry.

The constants C_1 and C_2 were determined in preliminary tests using calibrating liquids with known surface tension and density. As the calibrating liquids we used butyl and ethyl alcohols, acetone, hexane, and carbon tetrachloride of analytically pure grade. The value of h_3 was determined using a KM-8 cathetometer.

For the experiments we used potassium with purity 99.936%. The potassium was cleaned prior to filling the setup by filtering through a plate made from porous stainless steel and then by vacuum distillation.

Flame photometric analysis was used to detect the following impurities in the test metal: sodium 0.053%, rubidium 0.0006%, cesium 0.003%, calcium 0.002%. No change of the chemical composition of the metal during the experiments was observed.

The first series of tests was conducted in the following sequence (Fig. 2). The surface tension of the potassium at the boundary with its own vapor was first measured from 600 to 1126° C. Eleven experimental points were obtained for both increasing and decreasing temperatures; the points on the figure are numbered in sequential order. The measurements were made only after holding for a long time at a constant temperature. Good reproducibility of the experimental values was observed.

Then 99.975% pure helium was introduced into the upper chamber of the cylinder through a valve. The potasisum surface tension at the boundary with the helium was measured as the temperature was reduced from 682 to 77° C (points 12-18). In these experiments no marked influence of the helium on the potassium surface tension was observed, although the points began to deviate upward slightly.

Ten hours after reheating, the potassium surface tension at a temperature of 453° C began to increase and rose from 76.8 to 80.6 dynes/cm (points 19-23). Thus, only long-term contact of quite pure helium led to an increase of the surface tension values. Here the data practically coincide with those of [7].

The second series of tests was conducted using a new batch of potassium. Five experimental points were obtained at the boundary with its own vapor (24-28), which agreed very well with the data of the first series of tests obtained under the same conditions. This indicates that during the test time there was no

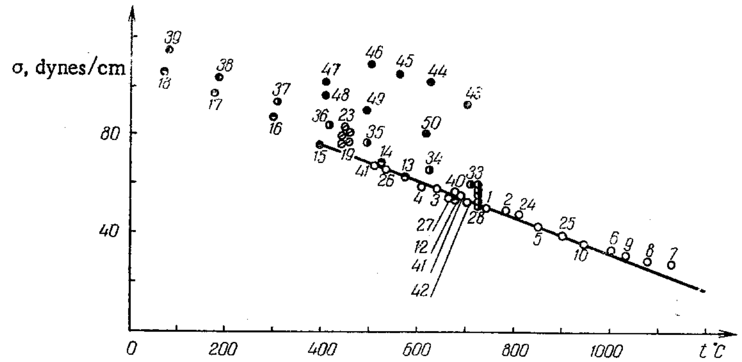

Fig. 2. Effect of inert gases on surface tension of potassium.

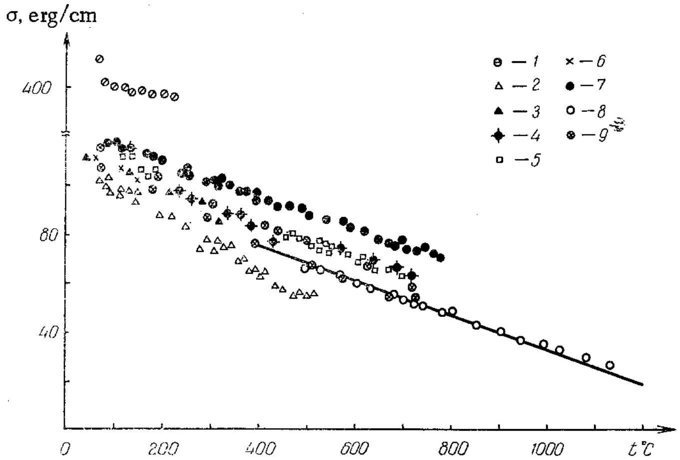

Fig. 3. Potassium surface tension values published in various studies and those of the present experiments: 1) [1]; 2) [4]; 3) [5]; 4 [6]; 5) [7]; 7) [8]; 7) [9]; 8) present study, in vacuuo; 9) present study, in helium.

contamination of the test metal by active impurities from the container. Then, just as in the first series of tests, helium (but less pure – 99.91%) was admitted again at a temperature of 717° C.

After an hour and a half the potassium surface tension increased by 12% (points 29-33), thereafter the value of σ stabilized. Then measurements were made of the potassium surface tension as the temperature was decreased from 622 to 80° C (points 34-39). Good reproducibility of the experimental data and very small scatter was observed. In essence we obtained a new curve which was equidistant from the first curve. The experiments were conducted for a long time and all the points continued to fall on this curve (nearly coinciding with the data of Bohdansky). It can be assumed that the surface layer of the metal was already saturated with either gases, oxides, or nitrides.

To verify this assumption the upper layer of metal and the gas were removed through the upper valve at a temperature of 78° C. The experimental data obtained after this at the boundary with its own vapor (points 40 and 41) agreed with the previous values obtained under the same conditions. This confirmed the assumption that the reason for the change of the potassium surface tension was the gas.

The third series of tests used argon (99.85% pure), introduced into the vapor phase of the metal at a temperature of 700° C. The experimental points 43-50 were obtained in the argon atmosphere, with the points 47-50 being obtained after reheating the metal. In this case the surface tension increase was still greater. The stabilized values agreed with the data obtained earlier by the vertical plate withdrawal method. In these experiments the surface of the metal was in contact with a large inert gas volume for a long time.

TABLE 1. Experimental Values of Potassium Surface Tension σ (dynes/cm)

t, °C	σ	t, °C	σ	t, °C	σ
First series					
503.4	67.47	1028.0	31.97	180.0	97.06
535.2	66.09	1085.0	28.71	78.9	105.81
609.0	58.99	1126.5	27.15	In helium atmosphere after reheating	
644.2	57.02	Second series			
688.0	54.84	669.0	54.52	449.5	80.63
701.3	52.57	717.1	51.63	453.8	79.70
737.0	49.69	682.0	54.30	708.8	59.28
788.0	46.57	In helium		622.0	65.69
804.8	48.15	682.1	54.10	495.2	76.22
853.0	41.97	573.0	62.66	418.0	82.33
903.0	39.56	520.2	67.31	304.0	92.40
948.1	36.34	396.2	77.08	192.2	102.61
997.2	34.75	298.0	85.60	77.8	113.28

We see from these experiments that the presence of helium and argon above the surface of the potassium melt caused an increase of the metal surface tension. This increase depends on the degree of purity of the gases used. We also see from Fig. 2 that the impurities present in the inert gases, while altering the absolute value of σ, have very little effect on the magnitude of the temperature coefficient $d\sigma/dt$. We can also conclude that the time in the course of which the metal is in contact with the gas is significant. Therefore it is quite possible that experiments using the method of the maximal pressure in the gas bubble yield good results because of the short contact time.

It is difficult to say at the present time just what the reason is for the surface tension increase. To this end future experiments must be made with different, precisely controlled additions of such gases as oxygen, nitrogen, CO_2, and so on. It is possible that oxygen is the cause (it was present to the largest degree).

In 1955 Addison [11] studied the influence of oxides on the surface tension of sodium. In his tests he found that for small magnitudes of the oxide contamination some reduction of the surface tension was observed, while with increase of the amount of oxides the value of σ increased. Addison explained this phenomenon by the fact that for small amounts of the oxides (below the solubility limit for the given temperature) the surface tension must decrease, since the oxide solution has a lower value of the surface tension. With increase of the amount of oxides the latter precipitate from the solution and may form a quite rigid film. The observed value of σ must increase. We can assume that the observed increase of the potassium surface tension in our tests was also caused by the presence of oxides and hydrides in the surface layer of the melt. The results of mass spectrometric analysis of 99.975% pure helium can serve as confirmation of this assumption. The analysis detected the following impurities in the helium: oxygen 0.01%, hydrogen 0.01%, nitrogen 0.002%, CO_2 0.002%. In Addison's experiments with sodium this amount of oxygen caused an increase of the surface tension. Thus, we can assume that the experimental data obtained in the atmosphere of the metals' own saturated vapors are the most reliable data.

The results of the described experiments agree to within experimental error with the data of Germer [8], points 6, who conducted experiments under very pure conditions. The data of Taylor [4], points 2, as has been noted repeatedly in the literature, are apparently in error (with respect to the temperature coefficient), and we can assume that the data of Bohdansky [7], points 5, are somewhat high because of the presence of gas. We have shown above that such high values can be obtained by using gas which is not sufficiently pure. The data of [9], points 7, lie still higher, and here the problem may be with both the gas and the presence of sodium, whose content in the test potassium reached 3%.

The table shows the experimental data of all the series of tests. The experimental points obtained in the saturated vapor atmosphere can be described in the first approximation by the linear equation

$$\sigma = 76.8 - 0.0703\ (t - 400^\circ)\ \text{dynes/cm}$$

which is valid from 400 to 1120° C. The mean square deviations from this equation amount to 1.8%. Upon careful examination of the pattern of the experimental points we can note that they are described more accurately by a concave curve.

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