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Analysis of the Heat of Breaking Glass Ampoules

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Synopsis. The heat of breaking was measured on three series of ampoules, containing N_2 at various pressures, N_2 at various pressures as well as saturated H_2O vapor, or different amounts of liquid H_2O as well as the saturated vapor in the unfilled space, respectively. This report gives the method to analyze the heat of breaking of ampoules into three factors: the release of mechanical strain stored in the ampoule under a pressure, heat of evaporation of immersion liquid, and rush-in effect of the liquid.

The heat of breaking of glass ampoules is one of the most troublesome problems in microcalorimetry such as for heat of immersion measurements, and it is quite serious when the solid has low surface energy or small surface area. Three causes have been considered for the heat of ampoule breaking:[1-3] (1) release of mechanical strain stored in the ampoule under a pressure, (2) heat of evaporation of immersion liquid due to the volume change on breaking, and (3) rush-in effect of the liquid, called the PV effect, when the ampoule is filled with the liquid after breaking. It has been reported that a major part of the heat of ampoule breaking is caused by the last effect;[4] it can be much reduced by filling up the ampoule with an inert gas like He.[1,5]

Here, we report the results of an experimental analysis of these three heat effects, from which we can establish the correction of the heat of breaking in microcalorimetry.

Experimental

The ampoules used here were commercial ones, which are cylindrical, having fairly uniform capacity of about 3 cm^3. Three series of sealed ampoules were prepared. The first series contained N_2 at various pressures, and the second series N_2 at various pressures which was saturated with H_2O. The third series contained different amounts of liquid H_2O and its vapor. Special precautions were taken for sealing off the ampoules so as to keep their volumes contant as close as possible. The average volume was 3.2 ± 0.1 cm^3. Measurements were made in H_2O at 28 ± 0.1 °C, in an adiabatic calorimeter equipped with a quartz thermometer as a temperature sensing element.[6] In order to avoid random breaking of ampoules, they were edged uniformly by a file around their circumference, and then were broken between steel knife edges, by using a screw.

Results and Discussion

Figure 1 shows the relationship between the heat of breaking and the N_2 pressure in the ampoule. For a series of ampoules containing N_2 and saturated H_2O vapor, the heat is plotted against the partial pressure of N_2. It is seen from Fig. 1 that heats of breaking of the ampoules containing both N_2 and saturated H_2O vapor are higher than those containing N_2 only, and both series of heat decreased linearly with increasing pressure of N_2 and in parallel with each other. This fact suggests that a constant amount of H_2O evaporates on breaking the ampoules containing N_2 only, which leads to a decrease in heat generation. This endothermic effect is 0.21 J, which is obtained from the difference between the two straight lines in Fig. 1. The heat of vaporization of H_2O into the space of 3.2 cm^3 at 28 °C can be calculated to be 0.212 J, which is in good agreement with the experimental value. Thus, it is understood that breaking of an ampoule in a liquid is accompanied by evaporation of the liquid, the volume of vapor formed being equal to that of the ampoule, except in the case where the ampoules contain saturated vapor of the immersion liquid, which results in partial cancellation of the heat evolved.

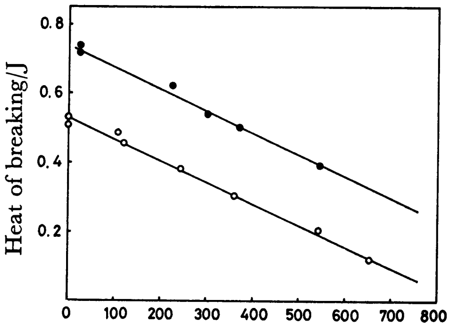

Fig. 1. Heat of breaking glass ampoules as a function of pressure of N_2, in the presence of N_2 only ○, and N_2 and saturated H_2O ●.

Figure 2 represents the heat of breaking when ampoules having different amounts of liquid H_2O were broken in H_2O. It is seen from Fig. 2 that the heat evolution decreases linearly with increasing amount of H_2O or decreasing space volume. Since the space in these ampoules always contains saturated H_2O, evapora-

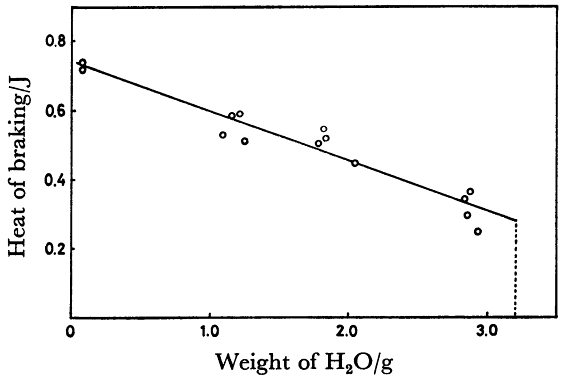

Fig. 2. Heat of breaking glass ampoules as a function of weight of H_2O contained.

tion of H_2O should not occur. Admittedly, both evaporation of H_2O and the rush-in effect of the liquid will disappear when the space volume is zero. In other words, we may consider the heat evolved in this limiting case to be equal to the heat due to the release of mechanical strain stored in the ampoule. This heat value can be obtained by extrapolating the straight line in Fig. 2 to the zero space volume and is found to be 0.28 J. It is easy to understand that the heat value changes with the variety of ampoules and also with the breaking modes.

As determined from Fig. 1, the heat of breaking of an ampoule, when it is empty, is 0.53 J. This value contains of course all the three effects of heat generation. By subtracting the heats due to evaporation of H_2O and the release of mechanical strain from the total heat effect 0.53 J, we obtain the heat due to the rush-in effect, 0.46 J. If we estimate the product of pressure difference between outside and inside the ampoule and its volume, we obtain 0.324 J, which is much less than the rush-in heat. This result suggests that the rush-in effect, formerly called the PV effect, is not only a static effect, but it also includes dynamic processes such as collision of the liquid stream with the glass wall, and of liquid masses with each other and friction of liquid when it rushes into the ampoule.

Further consideration leads to the conclusion that when ampoules containing both N_2 of 1 atm and saturated H_2O vapor are broken, only the effect of release of mechanical strain appear, because the rush-in effect disappears. In fact, the value 0.26 J from Fig. 1 is close to the value, 0.28 J, described above as the heat due to the release of mechanical strain. Thus, it can be understood that the difference of heat evolved under the conditions at both ends of every series of measurements, *i.e.*, at both ends of three straight lines (Figs. 1 and 2), represents the heat due to the rush-in effect; experimental values thus obtained from the three series of experiments are 0.48, 0.47, and 0.47 J, being quite close to each other. Therefore, the enclosure of He at 1 atm into an ampoule can avoid the rush-in effect of liquid in microcalorimetry, but does not eliminate the evaporation effect of the liquid.

Here, it is interesting to remember an ingenious method of Young and Bursh,[7] who broke several glass bulbs containing different weights of sample and extrapolated the results to zero sample content; the intercept was considered to be the heat of breaking the glass bulb, and the slope of the straight line to be the heat of immersion of sample. Strictly speaking, however, on the basis of the present analysis, the slope of the straight line should be the sum of three effects: the heat of immersion of the sample, the decreasing rush-in effect, and the decreasing evaporation effect, the last of which is endothermic.

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