THE VAPOR PRESSURE OF CARBONIC ACID.

BY JOHN ZELENY.

IN the May number of the PHYSICAL REVIEW Professor du Bois calls attention to a possible difference in the cryogenic properties of the snow obtained from commercial carbonic acid of different manufacture. He states that in their experiments for getting the vapor pressure of solid carbonic acid, he and Wills[1] used commercial gas which had been made from coke and contained at least 99.5 per cent. of carbonic acid with possible traces of air, water and grease.

As the results of some similar determinations made in this laboratory were published in this journal,[2] I wish to make some additional statements about the nature of the gas used. In the first place the gas coming from the cylinder was found to be perfectly odorless. In the experiments performed by Smith and me for determining the vapor pressure of liquid and solid carbonic acid at low temperatures, the gas was freed from its admixed air by allowing it to flow into a glass tube, the lower end of which was immersed in liquid air. The carbonic acid gradually froze at the bottom of this tube, while the air escaped. The gas obtained from this solid carbonic acid was almost completely absorbed by KOH, the residue being approximately one fortieth of one per cent.

I have since written to the company which supplied the gas, and they inform me that the gas was collected from fermenting vats and then passed in succession through four purifiers, each twenty feet high, the materials of which were copiously sprayed with water. The gas was then passed through calcium chloride on the way to the compressor. They inform me, further, that as shown by daily tests made at the factory, the gas obtained by this process is exceptionally pure, containing only a small amount of air and no traces of any vegetable substances.

[1] du Bois and Wills, Verh. der D. Phys. Gesell., I., p. 168.

[2] J. Zeleny and R. H. Smith, PHYS. REV., 24, p. 42; J. Zeleny and A. Zeleny, PHYS. REV., 23, p. 308.

It would thus appear that the gas we used was of good purity. The effect of any impurity upon the vapor pressure of a solid is somewhat uncertain, depending not only upon its nature but also upon whether it is just mechanically mixed with the substance or whether it forms a solid solution with it.

The experiments which I carried out with A. Zeleny show that neither alcohol nor ether added to carbonic acid snow so as to form a thick mush with it, affects its vapor pressure appreciably over a wide range of temperatures. The temperature-vapor pressure curve obtained with these mixtures, the temperature at any pressure being acquired by the evaporation of the carbonic acid, was found to agree well with the curve obtained by Smith and me where the pure solid carbonic acid was maintained at different temperatures by the aid of liquid air.

We used the temperature of a mixture of alcohol and carbonic acid as determined by Holborn,[1] in Berlin, with a hydrogen thermometer as one of the calibration points for our thermo-element, and the point on the calibration curve was in harmony with the other points used. The results obtained with our carbonic acid for the vapor pressure of the liquid up to 25 atmospheres pressure and for the solid for pressures above one atmosphere agree well with the results obtained by Kuenen and Robson[2] in Scotland. Such agreements point to the absence of deleterious impurities.

I agree with Professor du Bois that it is difficult to get the value of $dP/d\theta$ accurately at 76 cm. pressure from the experimental curves. The value of the tangent being in the neighborhood of 6, a change of $1°$ in the inclination of the curve at the desired place makes a change of about 10 per cent. in the tangent. Still, the error in drawing the curve with its true inclination is apt to be less where the experimental points extend a considerable distance to each side of the 76 cm. as they did in the case of Smith and myself, than where they end close to the 76 cm. point.

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[1] Holborn, Annal. der Physik, 6, p. 245.
[2] Kuenen and Robson, Phil. Mag. (6), 3, p. 149.