

have been due to properties inherent in the pipets which were of the same general type of metal but of different shape and cross section. The closer agreement in the case of the mixture may be due to the fact that the published values were the average results of a number of independent runs extending over a period of nearly two years.

The second group of error sources contains the more subtle factors such as (a) stress-strain relationship and volume change, (b) viscous and plastic flow and permanent set in steels, (c) temperature and volume change relationships, (d) chemical action of the gases on the pipet material, (e) solubility of the gases in the pipet material and (f) diffusion of the gases through the walls of the pipet. In view of the fact that this is but one of a series of investigations in this field, careful presentation of the complications resulting from the above disturbing factors seems justified.

(a) Love's formula, which has been used to calculate change in volume with change in pressure, was derived for cylinders, long in comparison to diameter. It neglects end effects. The cylinders used in this investigation have heavy walls which are subjected to stresses and strains of unknown magnitude due to the tension and compression effects of the plug at one end, as well as to internal stresses and strains due to the rolling of the metal and forging of the steels. However, as the calculated maximum change in volume with change in pressure is 0.13% even at 1000 atmospheres, the uncertainty introduced at temperatures to 300° should not exceed 0.05% in the final compressibility factors. Up to 300° the coefficient of elasticity of chrome vanadium steel remains constant to within 15%.<sup>11</sup> Between 300 and 400° the modulus falls rapidly, possibly as much as 40%. At 400° therefore a small additional error may be introduced.

(b) The phenomena of plastic and viscous flow and strain hardening assume importance only at the highest temperature (400°) used in this investigation. Alloys of the type used in the pipets have not been studied in relation to these phenomena. However, French<sup>12</sup> has found the elongation of 0.24% carbon steel at 430° to be 2.5% over a period of 300 hours under a constant load of 25,000 lb. per square inch, while 13% Cr stain resisting steel showed but a few tenths of a per cent. elongation under similar conditions. It appears that no appreciable error can be introduced by neglecting the small changes caused by these factors during the few minutes in which the stress in the pipet reaches 15,000-20,000 lb. per square inch. This conclusion is substantiated by the results of calibration of the pipet before and after use at high pressure and temperature. No difference in size of the pipet has been observed.

(c) The accuracy of the temperature capacity correction for the pipet depends entirely upon the accuracy of the equation in expressing the relation of temperature and capacity at temperatures to 400°. The temperature correction at 400° is 1.65%. An error of 6% in the correction would be required to introduce an error of 0.1% in results.

(d) Errors introduced through apparent change in capacity of the pipet through formation and subsequent decomposition of nitrides and hydrides in the walls of the pipet are apparently negligible. While the literature contains many references to

<sup>11</sup> French, *Bureau of Standards Technologic Paper No. 205*, 1921; also private communication from J. S. Vanick, formerly of the Bureau of Standards.

<sup>12</sup> French, "Methods of Test in Relation to Flow in Steels at Various Temperatures," Preprint, 1926, American Society for Testing Materials.

nitride formation when iron and pure nitrogen are brought together at temperatures above 600°,<sup>13</sup> Noyes and Smith<sup>14</sup> have shown that at 460° the dissociation pressure of iron nitride (formed by action of NH<sub>3</sub> on iron) is greater than 20,000 atmospheres. The nitrides of chromium and vanadium, if formed at all, at 400°, would be stable compounds without appreciable effect on the capacity of the pipet. Baur and Voerman<sup>15</sup> give the dissociation pressure of chromium nitride as about 100 mm. at 800°. Slade and Higson<sup>16</sup> report the dissociation pressure of vanadium nitride to be "not greater than 0.2 mm." at 1203°. There seem to be no stable hydrides of iron or the alloying metals. It is well known, however, that hydrogen forms hydrocarbons with the carbon in the steel at 475°, and this reaction may occur at lower temperatures. It is probable that the hydrogen within the pipet at high temperatures contains traces of hydrocarbons. The time of contact is short, and the effect on the compressibility measurements is believed to be negligible.

(e) (f) The phenomena of gas solubility in metals and the rate of diffusion are so closely allied in their practical effects that they will be considered together. Nitrogen is generally present in steel. Data available, all at pressures below 200 atmospheres, indicate that nitrogen is "absorbed" by iron at elevated temperatures.<sup>17</sup> The amount absorbed is reported to be from 0.004%<sup>18</sup> found in a reduced iron sponge after eighteen hours' treatment at atmospheric pressure and 450°, to 0.3% found by Andrews<sup>19</sup> in massive iron cooled from the molten condition after long treatment with nitrogen at 200 atmospheres' pressure. The gas absorbed at 450° seems to have been entirely reclaimed by the use of a vacuum pump and was probably "adsorbed" on the very large exposed surface, a surface roughly calculated to be  $2.5 \times 10^3$  sq. cm. to a gram of iron. At the higher temperatures the presence of nitrogen may be explained by solid solution, chemical combination with the alloying metals or the presence of hydrogen from some decomposable compound of hydrogen and subsequent catalytic formation of ammonia. Doubtless there are adsorption effects on the walls of the pipet. The exposed area, however, is of such magnitude (about 30 cm.<sup>2</sup>) that even should the adsorption be proportional to pressure at 1000 atmospheres, the amount of gas involved would be less than 0.005 cc. (S. T. P.) at 450°. At the lower temperatures the amount would be larger but should introduce no appreciable error even at 0°. Ryder<sup>20</sup> could detect no diffusion of nitrogen through steel at temperatures below 500°. Even at 1200° the diffusion rate is very slow. No appreciable error in the results of the present investigation should therefore arise from solubility and diffusion phenomena in the case of nitrogen.

Facts concerning the solubility and rate of diffusion of hydrogen through iron and steel are somewhat better established. It is well known that hydrogen released at an iron cathode of an electrolytic cell quickly penetrates to a considerable depth in the electrode, even at room temperature.<sup>21</sup> Diffusion of this nature is apparently due to the presence of atomic hydrogen. Similar diffusion effects due to thermal dissociation of

<sup>13</sup> Sawyer, *Trans. Am. Soc. Steel Treating*, 8, 291 (1925), a review with 60 references; Guillet, *Compt. rend.*, 182, 903 (1926).

<sup>14</sup> Noyes and Smith, *THIS JOURNAL*, 43, 475 (1921).

<sup>15</sup> Baur and Voerman, *Z. physik. Chem.*, 52, 473 (1905).

<sup>16</sup> Slade and Higson, *J. Chem. Soc.*, 115, 215 (1919).

<sup>17</sup> From an unpublished report of the Fixed Nitrogen Research Laboratory.

<sup>18</sup> Andrews, *Engineering*, 94, 860 (1912).

<sup>19</sup> Ryder, *Elec. J.*, 17, 161 (1920).

<sup>20</sup> Schmidt and Lucke, *Z. Physik*, 8, 152 (1922); Edwards, *J. Iron Steel Inst.*, (advance proof), Sept., 1924; *C. A.*, 18, 3348 (1924); Bodenstein, *Verhandl. deut. physik. Ges.*, 3, 40 (1922).