FIG. 1.—Graph of ln (x_2/x_2^0) against the density for the system carbon dioxide + air.[8]
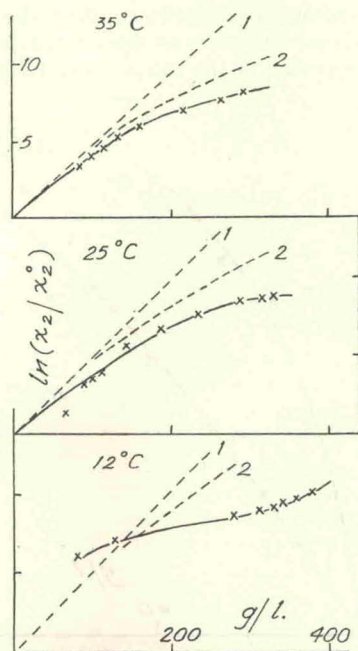

FIG. 2.—Graph of ln (x_2/x_2^0) against the density for the system naphthalene + ethylene.[9]
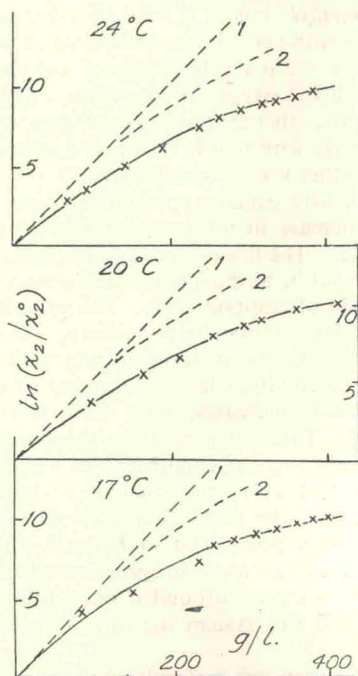

FIG. 3.—Graph of ln (x_2/x_2^0) against the density for the system hexachlorethane + ethylene.[10]
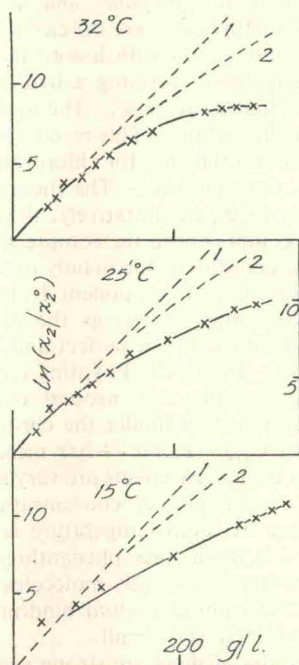

FIG. 4.—Graph of ln (x_2/x_2^0) against the density for the system p-chloro-iodo-benzene + ethylene.[11]

Full line, experimental; dashed line (1), calculated from first term of (2.8); dashed line (2), calculated from first two terms of (2.8).

experiment is excellent. Both the initial slope and the curvature of the experimental line are well reproduced. It is concluded that in this simple system the properties of the solution can be calculated satisfactorily from the properties of the pure substances alone.
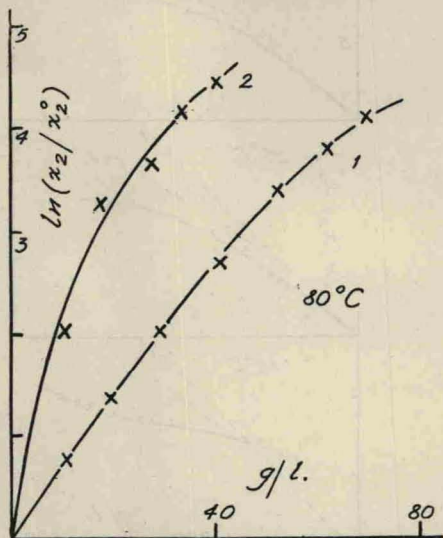

FIG. 5.—Graph of ln (x_2/x_2^0) against the density for the systems iodoform + propane (curve 1) and iodoform + dimethyl ether (curve 2).

Naphthalene + ethylene (Diepen and Scheffer [9]).—The experimental and theoretical curves are shown in fig. 2. The agreement between theory and experiment is not now so exact. At 35° C the agreement is satisfactory except at the highest densities, but it becomes worse as the critical temperature of ethylene (9° C) is approached. This is not unexpected as the virial equation of state breaks down at this point.

Hexachlorethane + ethylene (van Gunst [10]) and p-*chloro-iodobenzene + ethylene* (Ewald [11]).—These are the two systems in which the critical constants of the solids are known only approximately. Fig. 3 and 4 show that agreement is only qualitative. At high densities the increased curvature of the experimental lines is probably due to the higher terms in (2·8) which have been neglected in these calculations.

Iodoform + propane and iodoform + dimethyl ether (Ewald [11]).—Propane and dimethyl ether are iso-electronic molecules with very similar critical constants. Their interaction with iodoform was studied to see if the hydrogen of iodoform was capable of forming a hydrogen bond with the oxygen of the ether. Fig. 5 shows that is the case. The interaction with the ether is much greater than with the hydrocarbon. This result agrees qualitatively with that of Fox and Lambert [5] who found that B_{12} for chloroform + diethyl ether was unusually large.

5. CONCLUSIONS.—The theory put forward here explains qualitatively, and in simple cases, quantitatively, the very great increase in the concentration of the solid component in the compressed gas mixture. The linear increase in ln (x_2/x_2^0) at low densities is due mainly to the term B_{12}, that is, to the independent clustering of molecules of component 1 about a molecule of component 2. The solubility increases more slowly as the density rises. This is due to two effects. First, the added gas is not perfect and so its pressure does not increase linearly with its density. Hence the Poynting term is lower. Secondly, when the number of gas molecules clustering around one solid molecule increases, then their mutual interactions will hinder the clustering process. This is expressed by the positive sign of C_{112}. Robin [12] has measured the solubility of phenanthrene in nitrogen where both these effects are very small, and so ln (x_2/x_2^0) is proportional to density up to much greater concentrations than usual. The first effect is small since nitrogen at room temperature is near to its Boyle point, and so $B_{11} \approx 0$. The second is small since phenanthrene is a large molecule and nitrogen a small one, and so more nitrogen molecules than usual can cluster around a phenanthrene molecule without mutual hindrance. That is, in this system the ratio C_{112}/B_{12}^2 is apparently very small.

Finally, if there are strong specific forces between one molecule of the gas and one of the solid then the initial slope of ln (x_2/x_2^0) will be greater than the principle of corresponding states would indicate.