Table 2. DATA OF NAKAMOTO *et al.* USED IN RECTILINEAR CORRELATION IN FIG. 1

Compound	Type of hydrogen bond	O....O distance (Å)	$\nu_{OH}(cm^{-1})$
Nickel complex of salicylaldoxime	Intramolecular	2·45	3,270
2-Nitroresorcinol	Intramolecular	2·50	3,280
Salicylic acid	Intramolecular	2·59	3,225
Salicylaldehyde	Intramolecular	2·60	3,100
Methyl salicylate	Intramolecular	2·60	3,220
Catechol	Intramolecular	2·75	3,333
$(COOH)_2.2H_2O$	Intermolecular	2·88	3,460
$LiOH.H_2O$	Intermolecular	2·99	3,570
NaOH	Intermolecular	3·02	3,571
$Cu(OH)_2$	Intermolecular	3·36	3,690

The change in slope at 2·8–2·9 Å of the solid line for intermolecularly hydrogen bonded compounds suggests that at O....O distances shorter than this some new interaction becomes significant. Pauling[5] and Coulson and Danielsson[6] have shown that as the O....O distance becomes less, the covalent or delocalization contribution to the energy of the hydrogen bond becomes greater. On this interpretation Fig. 1 suggests that covalent contributions to hydrogen bonding energies are negligible at O....O distances greater than 2·8 2·9 Å and also that covalent contributions are negligible for most bent (that is, intramolecular) hydrogen bonds. This is not unreasonable since orbital overlap will be greatly hindered by lack of collinearity in the hydrogen bond. Support for this view is given by a previous investigation[7] of nitro stretching frequencies in 2-nitrophenol, which indicated that the intramolecular hydrogen bond in this compound is electrostatic in nature.

Displacement of a point such as that representing salicylaldehyde from the broken line towards lower frequency may indicate some degree of covalency in the hydrogen bond in this compound[7].

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Influence of Ambient Gases on the Rate of Evaporation of Water

IN a recent communication, W. W. Mansfield[1] has described some new experiments on the rate of evaporation of water, from which he has concluded that in work on this subject by Sechrist[2] and by Kingdon[3] the observed effects were influenced more by buoyancy than by any other factor. Hitherto the evaporation of water from a source at fixed temperature, say 50° C, in a quiescent, ambient gas with the total pressure of about 1 atm., has been considered to be principally determined by the rate of diffusion of water vapour through the ambient gas, although it has been recognized that there must be also a hydrodynamic flow of gas and vapour away from the evaporating surface (the Stefan flow[4]), which has its origin in the diffusion of the ambient gas under its concentration gradient near the water surface. The Stefan flow is the probable reason for the departure of the rate of evaporation of water from linearity with the vapour pressure in the comprehensive experiments of Boelter *et al.*[5]. Mansfield's conclusion would add a gravitation-controlled process to these two diffusion-controlled processes.

Although experiments on the evaporation of drops are admittedly subject to several disturbing effects, it appears that the most careful experiments are in too close agreement with diffusion theory to permit the presence of a significant gravitational effect. Thus in the very thorough work of Langstroth *et al.*[6] on the evaporation of droplets of water (radius about 0·06 cm) in air (690 mm mercury) at ambient temperatures of 10, 20, and 40° C, the agreement with theory was within 5 per cent. The theory included an approximate correction for the Stefan flow (maximum about + 1 per cent). The most important disturbing effect was the cooling of the drops by evaporation which reduced their actual surface temperatures (average of two methods) to about −1·0, +4·5, and +12·7° C respectively.

Langstroth *et al.*[6] also examined the evaporation of toluene drops (radius 0·073 cm) into ambient air at 20° C, and obtained agreement with theory within about 1 per cent. The actual temperature of the drop was estimated at 11·0–11·4° C (two methods). Toluene has a vapour pressure of 13 mm at 11° C, and a molecular weight of 92·1, so that the density of the toluene-air mixture at the toluene surface (assuming no effect of air on the toluene liquid bonding) would be 1·04 times that of air. Similarly, if Mansfield's water drop was at 10° C in hydrogen at 20° C, the density of the water-hydrogen mixture at the water boundary would be 1·09 times that of hydrogen. If Mansfield's large effects in hydrogen (+70 per cent, −50 per cent) were due to a gravitational effect, it is surprising that no substantial effects from this cause complicated the results of Langstroth *et al.* with toluene.

Mansfield's experiments are described so briefly that any suggestion of another cause for his results must be very tentative, although variation in heat transfer to the drop is a likely candidate. If he worked with a hemispherical drop on the end of a glass tube, it seems likely that the transfer of heat from the gas to the drop would be substantially different in the upright and inverted positions of his flask. The importance of convection currents would also depend critically on the size of his flask[6].

In view of these considerations it appears that gravitational buoyancy effects have not been established as a major cause for the observed influence of ambient gases on the rate of evaporation of water.

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DR. KINGDON considers that generally the evaporation of water into a surrounding gas subjected to a minimum of external disturbance is determined principally by the diffusion of water vapour, and suggests that the experimental results of Boelter, Gordon and Griffin[1] may be interpreted accordingly.

Boelter *et al.* measured the rate of evaporation from a water surface placed flush with the floor of an air chamber, with the water surface maintained at a known but adjustable temperature greater than that of the surrounding air. The density of the air-vapour mixture at the surface differed from that found at some distance to an extent determined by the differences in temperature and in water-vapour content. Boelter *et al.* considered the