normally prevails in pure water, and partly on the mobility of the macromolecules on which the water is solvated. At the lower starch concentrations the most important change on gelling is an increase in hydration due to the swelling of the granules. At the high concentration any effect on gelation due to increased hydration is more than offset by the increased mobility of the macromolecules, which causes a narrowing of the water band.

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The 'Irving-Williams' Order in the Metal-ligand Stretching Frequencies of Some Metal Hydrazine Complexes

MANY infra-red spectra of metal complexes have been examined in the 2–15 μ region, but until now very few co-ordination compounds have been studied in the caesium bromide region in which some metal-ligand atom-stretching frequencies are expected¹. Furthermore, no correlation between the frequency of this vibration and the nature of the metal has been found².

We have measured the infra-red absorption spectra in the 15–35 μ zone of the hydrazine complexes of the 3d sub-group metals of the general formula $M(N_2H_4)_2Cl_2$. The two bands in the 660–518 and 440–343 cm^{-1} regions have been assigned to the N_2H_4 rocking and to the $M-N$ stretching vibrations, respectively. The sequence of these frequencies agrees closely with the 'Irving-Williams' order of the stability of bivalent metal complexes: manganese < iron < cobalt < nickel < copper > zinc (ref. 3).

In Table 1 the observed infra-red frequencies are recorded.

It is interesting to compare such frequencies with the strengths of the $M-N$ bonds in complexes having four such co-ordinate links. As a measure of the bond energy, the heats of formation in aqueous solution of the bis-ethylenediamine metal ions, $M(en)_2^{2+}$ (ref. 4), have been used (Fig. 1). The $M-N$

Fig. 1. Graph of the N_2H_4 rocking (□) and $M-N$ stretching (○) frequencies versus the heats of formation of $M(en)_2^{2+}$ complex ions

stretching and the N_2H_4 rocking frequencies plotted against the ΔH_{1-2} values lie on two straight lines.

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Analogy to the Kirkendall Effect in the Gas Phase

THE Kirkendall effect¹ was first observed as a movement of fine molybdenum wire markers in a contact plane between brass and copper during interdiffusion. If diffusion occurs by a random walk movement of individual atoms, then, no matter what theory is employed for their detailed motion, it is difficult to see how it could produce movement of markers. Darken² considered that diffusion of copper and zinc occurred in opposite directions, at independent rates, and that the difference was compensated by a 'bulk flow'. If it fails to occur, voids are left behind by the more rapidly moving component, and this result of diffusion in metals has in fact been observed³.

The concepts used by Darken were also developed by Hartley and Crank⁴ for liquids, and their consequences have recently been studied in this Laboratory⁵. Lately, however, Adamson⁶ failed to observe the Kirkendall effect in liquids, using colloidal particles as markers in sucrose solutions. Now, as Darken's concepts do not depend upon mechanism, they should be equally applicable to solids, liquids and gases⁷, and we decided therefore to find if the Kirkendall effect could be demonstrated in gases.

A Loschmitt cell was used consisting of two glass cylinders (4 in. diameter, 7 in. length) which were sealed into two circular plane steel plates. By turning one plate over the other, the gases formed a diffusion boundary of sufficiently large area to make wall effects negligible. The gases used were CF_3Cl and hydrogen, to give widely different diffusion-rates. As

Table 1. N_2H_4 ROCKING AND $M-N$ STRETCHING FREQUENCIES FOR $M(N_2H_4)_2Cl_2$ COMPLEXES

Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Type of vibration
518	554	582	613	660	580	N_2H_4 rocking
343	369	388	409	440	385	$M-N$ stretching