

The quadratic formalism of Darken¹⁶ proposes that in general $g_1^E = aX_2^2$ and $g_2^E = aX_1^2 + \text{const.}$ for solutions rich in component 1, with analogous behaviour at the other terminal region. Clearly the AgCl + Ag₂S melts fit the Darken description, with S_i^E exhibiting similar behaviour to g_i^E , as shown in fig. 4. The structural interpretation of the quadratic formalism is that in the AgCl-rich solutions the

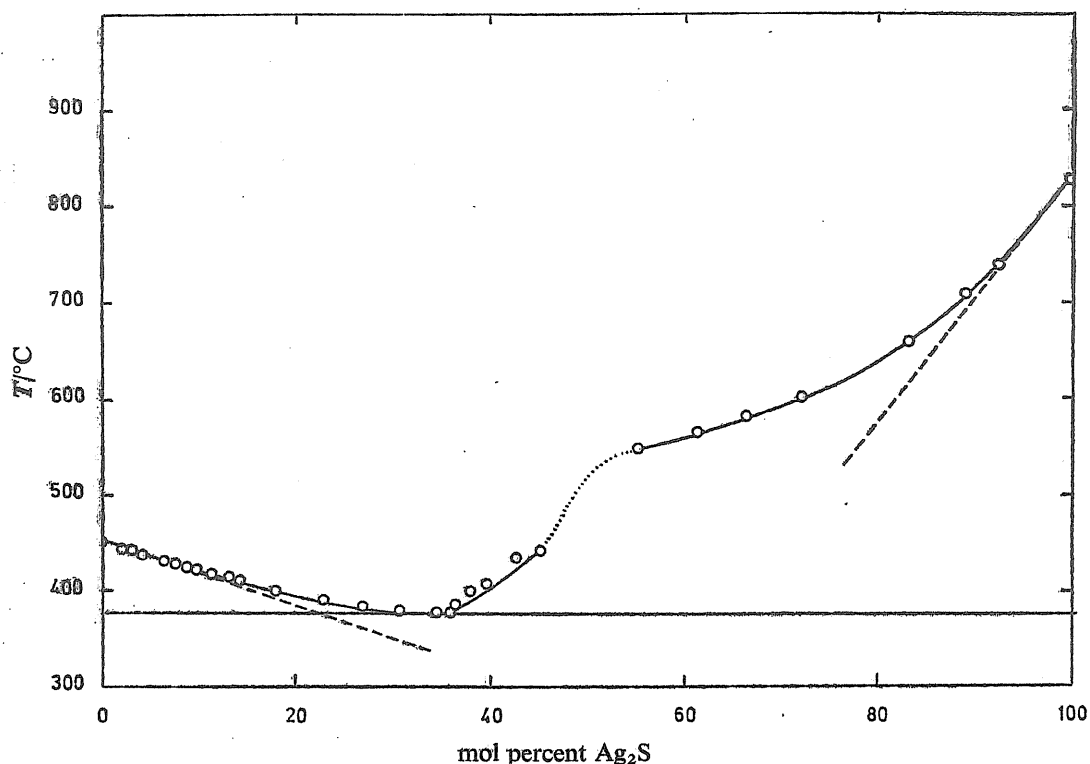


FIG. 2.—AgCl + AgS phase diagram¹ plus the theoretical "one foreign particle" limiting slopes calculated from the new ΔH_f value¹² (see text).

TABLE 2.—THERMODYNAMIC DATA FOR AgCl + Ag₂S MIXTURES

$10^{-2} X_{Ag_2S}$ %	T_{liquidus}/K ¹	g_i^E on liquidus /J mol ⁻¹ ³	Δh_i /J mol ⁻¹ ³	$S_i^E = \frac{\Delta h - g_i^E}{T_{\text{liq}}}$ J K ⁻¹ mol ⁻¹	$(g_i^E)_{800}$ from $\Delta h_i - 800.S_i^E$ /J mol ⁻¹	
0.0	726	0	0	0	0	} $i = \text{AgCl}$
0.1	696	63	55	-0.02	54	
0.2	672	264	200	-0.09	276	
0.3	658	711	404	-0.46	774	
(0.4) extrapolated	647	1305	639	-1.05	1477	
(0.3) extrapolated	623	2594	1046	-2.47	3021	} $i = \text{Ag}_2\text{S}$
0.4	681	1987	602	-2.05	2243	
0.5	773	1950	310	-2.13	2017	
0.6	837	1536	130	-1.67	1469	
0.7	869	908	38	-1.00	841	
0.8	921	410	0	-0.46	368	
0.9	984	13	0	0.00	0	
1.0	1103	0	0	0	0	

structure of AgCl is maintained, while in Ag₂S-rich solutions the structure of Ag₂S is maintained. There is a narrow transition region between $X_{\text{AgCl}} = 50\%$ and $X_{\text{AgCl}} = 60\%$ in which the structure changes. The extreme narrowness of this transition region in this system is particularly noteworthy. The negative values of S_i^E indicate an ordered structure.

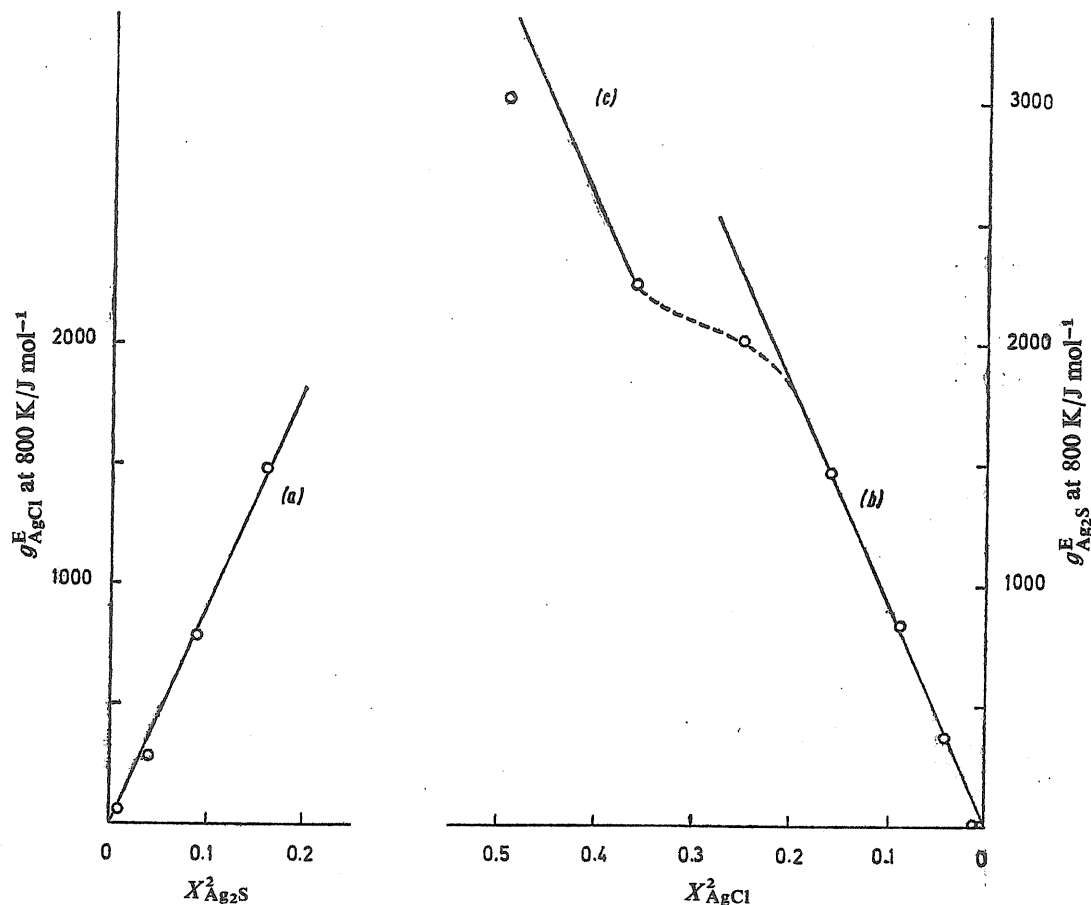


FIG. 3.— g^E for AgCl+Ag₂S mixtures at 800 K showing terminal regions where $g_{\text{AgCl}}^E = 9100 X_{\text{Ag}_2\text{S}}^2 \text{ J mol}^{-1}$ [curve (a), $g_{\text{Ag}_2\text{S}}^E = 9260 X_{\text{AgCl}}^2 \text{ J mol}^{-1}$ [curve (b)] and $g_{\text{Ag}_2\text{S}}^E = 9100 X_{\text{AgCl}}^2 - 1033 \text{ J mol}^{-1}$ [curve (c), calculated from Gibbs-Duhem relation and curve (a)]. The transition region is dotted.

THALLOUS CHLORIDE+THALLOUS SULPHIDE MIXTURES

The limiting one foreign particle liquid (fig. 1) agree with the experimental data in the dilute solution limit, as was found for the silver salts (fig. 2). In both systems, in infinitely dilute solution, each M_2S ($M = \text{Ag}$ or Tl) species adds one foreign particle to the chloride solvent (*e.g.* S^{2-} ion, M_2S molecule . . .) and *vice versa* for the sulphide limit. This behaviour contrasts with that of Cu_2S in CuCl melts, where (Cu_2S) dimers are indicated,⁶ and with Bell and Flengas' earlier analysis,¹ in which they found two foreign particles for dilute solutions of AgCl in Ag₂S calculated from their limiting slopes using the older ΔH_f values.

It seems reasonable to assume that, in the sulphide solvents, the chlorides are dissociated. Hence, the foreign particle in the sulphide solvents is the Cl^- ion. It then follows that the Tl^+ (or Ag^+) cations are incorporated into the Tl_2S (or Ag_2S) structures, and are not "foreign".