

## Effective molecular weights of the components in solution for the system anorthite-åkermanite

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**SUMMARY.** From thermodynamic considerations of the system anorthite-åkermanite it appears that the effective molecular weights of the 'molecules' in the melts of this system are 0.5 the molecular weights of anorthite as well as that of åkermanite.

The effective molecular weight value of 0.5 anorthite is in significant contrast to that of 1 anorthite obtained by Adams and Cohen (1966) from a similar analysis of the system anorthite-diopside (Bowen, 1915, and Osborn, 1942). The analysis by Adam and Cohen would lead to a non-ionic silicate melt structure in the system anorthite-diopside in contrast to the accepted electrolytic view of silicate melts. It is suspected that the reason for this apparent difference lies in the published liquidus morphology of the anorthite primary fields of the system anorthite-diopside. This same liquidus morphology is also responsible for the distortions in the isofracts and isotherms in the high-temperature area of the primary field of anorthite of the system anorthite-åkermanite-diopside (de Wys and Foster, 1958).

THE system anorthite-åkermanite is a join in the ternary system diopside-anorthite-åkermanite (de Wys and Foster, 1958), which exhibits a somewhat distorted geometry of the isofracts and isotherms in the high-temperature region of the anorthite primary field.

It was felt that an additional thermodynamic analysis of the binary system anorthite-åkermanite would perhaps yield additional insight into the reasons for the distortions as well as the molecular configuration of silicate melts. Earlier analytical results, based on the standard freezing-point lowering equation, revealed a typical electrolyte silicate melt solution with a van't Hoff factor of two and also that the system behaved quite ideally (de Wys, 1960a).

The thermodynamic technique used by Adams and Cohen (1966) to determine the 'effective molecular weights',  $M^*$ , of various other silicate binary systems indicated that anorthite in solution demonstrates effective molecular weight values of one (non-electrolytic), to one-half (electrolytic), that of the molecular weight,  $M$ , of crystalline anorthite.

Such a variation of an anorthitic silicate melt structure presents significant difficulties to previous deductions on the structure of silicate melts (de Wys, 1960a, b, c, d). A similar analysis to determine the effective molecular weights of anorthite as well as åkermanite was therefore performed on this 'ideal' binary system in order to compare

its results with those obtained by Adams and Cohen on anorthite in other less 'ideal' systems.

The analysis was based on the liquidus configurations of the system anorthite-åkermanite (de Wys and Foster, 1956) and on the same three equations summarized by Adams and Cohen as:

$$\Delta H_1 = -RT^2(dx_2/dT)/M_2^*x_1 \quad (\text{modified Gibbs approximation, MGA}),$$

$$\Delta H_1 = -RT^2(dN_2/dT)/M_1^*N_1 \quad (\text{Raoult approximation, RA}),$$

$$\Delta H_1 = -RT^2(dx_2/dT)/M_2^*x_1^2 \quad (\text{Gibbs approximation, GA}).$$

For these relationships  $\Delta H_1$  is the heat of fusion of the solid component plus the enthalpy of mixing to form the liquid solution,  $T$  is the absolute temperature of the liquidus in the primary phase region,  $N$  is the mole fraction,  $M^*$  is the effective molecular weight of the component,  $x$  is the mass fraction of the particular component while  $R$  is the gas constant. The suffixes 1 and 2 relate to the solvent and the solute components, respectively. The above relationships are based on the assumption of absence of isomorphism in the solid state but complete solubility in the liquid state.

The wide  $\Delta H_1$  ranges of values for anorthite and åkermanite are 375 to 505 J/g and 315 to 445 J/g respectively listed by Goranson (1942) and used previously by de Wys (1960a). The binary system anorthite-åkermanite may be regarded as practically ideal since the molecular volumes are nearly equal (Wagner, 1952). In addition if the heat of mixing of these two silicates is indeed small the ratio of these enthalpies of fusion should approximately equal the product of the ratio of their respective primary field liquidus slopes at the eutectic point and the inverse ratio of these eutectonic mass fractions (Dahms, 1898). The ratio of their average enthalpies is 0.8636 while the above product calculates to be 0.8731, which reinforces the conclusion that the binary system anorthite-åkermanite is ideal since the heat of mixing is negligible. Hence,  $\Delta H_1$  will then represent only the latent heat of fusion of the solid component.

The results of the analysis based on the above three equations are indicated in tables I and II. In table II, column 3 gives the ratio  $M^*/M$ , for each of the three equations, averaged over the four compositions of primary liquidus phase. It appears from these tables, therefore, that the 'effective molecular weights' of anorthite and åkermanite in solution are approximately 0.5 anorthite (i.e. 139.07) and 0.5 åkermanite (i.e. 136.33) respectively. Column 5 of table II gives the corresponding values of the van't Hoff factor  $i = M/M^*$  (Kirkwood and Oppenheim, 1961). These values agree well with the previously deduced van't Hoff factor of 2 (de Wys, 1960a) indicating an electrolytic silicate melt structure and in agreement with an ionic group concept (de Wys 1960a, d).

*Discussion.* These results compared with that obtained from the system anorthite-diopside by Adams and Cohen would indicate a controversial situation in that the 'effective molecular weight' of anorthite in its primary field of the system anorthite-åkermanite-diopside would therefore vary from 0.5 anorthite, revealing the expected electrolytic behaviour, near the join anorthite-åkermanite, to 1 anorthite, indicating a non-electrolytic silicate melt structure, near the join anorthite-diopside. This latter

TABLE I. *Ratio of effective molecular weight to formula molecular weight deduced from the binary liquidus*

Liquidus primary phase	Weight fraction of the primary phase	Liquidus temp. (°K)	Freezing-pt. lowering eqn used	$\Delta H_1$ joules gm	$\frac{M^*}{M}$		Average value $\frac{M^*}{M}$					
					An	Åk	An	Åk				
Åkermanite	1.00	1735	GA	315	0.6538	—	0.5569	—				
				445	0.4601							
			MGA	315	0.6538	—			0.5569	—		
				445	0.4601							
			RA	315	—	0.6501					—	0.5551
				445	—	0.4602						
	0.95	1710	GA	315	0.5927	—	0.5062	—				
				445	0.4196							
			MGA	315	0.5778	—			0.4934	—		
				445	0.4089							
			RA	315	—	0.5775					—	0.4931
				445	—	0.4087						
0.90	1698	GA	315	0.6537	—	0.5582	—					
			445	0.4627								
		MGA	315	0.6957	—			0.5941	—			
			445	0.4924								
		RA	315	—	0.6701					—	0.5723	
			445	—	0.4744							
0.85	1668	GA	315	0.7234	—	0.6223	—					
			445	0.5121								
		MGA	315	0.6662	—			0.5689	—			
			445	0.4716								
		RA	315	—	0.6699					—	0.5721	
			445	—	0.4742							
Anorthite	1.00	1826	GA	375	—	0.7176	—			0.6253		
				505	—	0.5329						
			MGA	375	—	0.7176	—	0.6253				
				505	—	0.5329						
			RA	375	0.7192	—	0.6267		—			
				505	0.5341							
	0.95	1803	GA	375	—	0.6128				—	0.5340	
				505	—	0.4551						
			MGA	375	—	0.5972		—		0.5204		
				505	—	0.4435						
			RA	375	0.5834	—	0.5084	—				
				505	0.4333							
0.90	1788	GA	375	—	0.7599	—			0.6622			
			505	—	0.5644							
		MGA	375	—	0.7366	—				0.6418		
			505	—	0.5470							
		RA	375	0.5999	—	0.5227	—					
			505	0.4455								
0.85	1760	GA	375	—	0.6990			—	0.6091			
			505	—	0.5192							
		MGA	375	—	0.6437			—		0.6080		
			505	—	0.4779							
		RA	375	0.5807	—	0.5060	—					
			505	0.4312								

value although correctly obtained by Adams and Cohen appears certainly unusual especially since Martin and Derge (1943) in experimenting with silicate liquids of anorthite composition indicate that the calcium migrated to the cathode while a complex alumina silicate moved to the anode. They concluded, therefore, that in the

TABLE II. *Average effective molecular weights and van't Hoff (i) values obtained by RA, MGA, and GA methods*

Component	Freezing-point lowering equation used	$M^*/M$		$i = M/M^*$	
		Average	Grand mean	Average	Grand mean
Anorthite	RA	0.57	} 0.55	1.852	} 1.818
	MGA	0.55		1.818	
	GA	0.56		1.785	
Åkermanite	RA	0.55	} 0.57	1.818	} 1.754
	MGA	0.60		1.666	
	GA	0.61		1.639	

molten silicate such a composition is present as  $\text{Ca}^{2+}$  and a complex silico-aluminate ion resulting in a van't Hoff factor of two.

For the system forsterite-anorthite, however, a similar analysis by Adams and Cohen revealed the expected value of 0.5 anorthite for the 'effective molecular weight' of anorthite in the silicate melt.

The above analyses and the resulting contradiction concerning the molecular structure in the silicate melt would indicate that the system diopside-anorthite exhibits an unusual liquidus morphology responsible for the effective molecular weights deduced by Adams and Cohen.

The aforementioned distortions on the anorthite-diopside side of the diagrams of the isofracts and isotherms of the system diopside-anorthite-åkermanite would substantiate this view concerning the anorthite liquidus morphology. The concept that the silicate liquid in the primary field of anorthite would have effective molecular weights ranging from 0.5 anorthite (electrolytic) on one side of the primary field to 1 anorthite (non-electrolytic) on the other appears most unlikely.

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