general, successive dehydration boundaries tend to become steeper at low temperatures, a result of the increasing departure of water from ideal behaviour at low temperatures (Ellis and Fyfe, 1957).

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The following examples will illustrate such effects. From the data of Appendix 2 the  $\Delta V$ 's of reaction for the following have been calculated at 25°C.

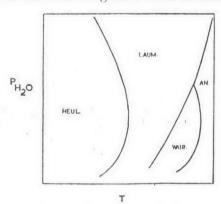


Fig. 6. Possible form of phase relations between heulandite, laumontite, wairakite and anorthite based on volume relations.

(2) 
$$\begin{array}{ccc} \operatorname{CaAl_2Si_4O_{12}.4H_2O} \to \operatorname{CaAl_2Si_4O_{12}.2H_2O} & + \ \operatorname{2H_2O} \\ & & \text{laumontite} & \to & \text{watrakite} & + & \text{water} \\ \Delta V = & +22 \ \mathrm{cm^3} \end{array}$$

(3) 
$$\begin{array}{cccc} \operatorname{CaAl_2Si_4O_{12}.2H_2O} \to \operatorname{CaAl_2Si_2O_8} + 2\operatorname{SiO_2} + 2\operatorname{H_2O} \\ & & \text{wairakite} & \to & \text{anorthite} & + & \text{quartz} & + & \text{water} \\ & & \Delta V = -10 \text{ cm}^3 \end{array}$$

These values assume a water density of unity; as equilibrium occurs at low temperatures, the values so calculated could be meaningful at moderate pressure. In a normal dehydration series  $\Delta V$  is positive for each step. This is obviously not the case in the above series and examples of negative boundary slopes and restricted low pressure fields (e.g. wairakite) are to be expected (Fig. 6).

Experimental studies are usually limited at low temperatures to pressures equal to or higher than the vapour pressure of liquid water. As boundaries pass through the two-phase region of water the slopes must change rapidly, but above this region they will be steep over a wide range of pressure.

## 4.4. Entropy of analcime

Fyfe et al. (1958) have discussed some general features of entropies of silicates