

Table 1. DIRECT TITRIMETRIC DETERMINATION OF MAGNESIUM IN SYNTHETIC SOLUTIONS

Mgm. present $\gamma$	Ion added $\gamma$	Mgm. found* $\gamma$	Difference $\gamma$
5	—	5	0
5	—	6	1
10	—	10	0
10	—	9	1
25	—	23	2
25	—	23	2
50	—	49	1
50	—	50	0
100	—	99	1
100	—	100	0
50	Cu-25	56†	6
50	Cu-25	50‡	0
50	Cu-50	50‡	0
50	Cu-50	50‡	0
100	Fe-50	100‡	0
100	Fe-100	98‡	2
100	Fe-100	98§	2

\* Procedure includes 10 ml. Clark and Lub's buffer pH 9.0, plus 15 ml. absolute methanol, plus 10 ml. magon (0.10 mgm./ml. MeOH). The solution is adjusted, if necessary, to pH 10.5 and then titrated with 0.005 *N* ethylenediamine tetraacetate.

† End-point fades, no cyanide present.

‡ 1-3 mgm. potassium cyanide added prior to addition of magon.

§ 1-3 mgm. ascorbic acid added prior to potassium cyanide.

solution should be made since large amounts slightly decrease the sensitivity of the colour-change. A buffer system, ammonium hydroxide-ammonium chloride, was unsatisfactory because of decreased sensitivity of the end point. Borate and tetraborate appear to increase a sharp colour change. Magon, essentially insoluble in water, is soluble in ethanol and methanol. Therefore the compound is dissolved in methanol and more methanol is added to the solution to be titrated. The concentration of alcohol in the solution to be titrated should range between 30 and 80 per cent. The indicator should be made fresh daily. Methanol is preferred since some decreased end-point sensitivity is encountered when using 95 per cent ethanol.

For this titration a pH-range of 9.0-11.0 is necessary. Clearest colour-changes are from pH 10.0 to 10.5. In the standardization of ethylenediamine tetraacetate with magnesium, the pH should be adjusted accurately to a selected pH within 10.0-10.5 and this same pH maintained for all titrations with the standardized titrant.

Under the above conditions the titration can be used for determining the combined amounts of calcium and magnesium, since calcium is titrated before magnesium. Calcium may be separated from magnesium as the precipitated calcium tungstate<sup>7</sup>. Preliminary results in this laboratory show magon to be very sensitive for the determination of total hardness of waters.

The possible usefulness of this new, sensitive indicator, or its magnesium complex, in the titration of micro-amounts of other metals should not be overlooked<sup>8</sup>.

I wish to acknowledge the technical assistance of Neil Scott McNutt.

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Dec. 23.

<sup>1</sup> Mann, C. K., and Yoe, J. H., *Anal. Chim. Acta*, **16**, 155 (1957).

<sup>2</sup> Drosdoff, M., and Nearpass, D. C., *Anal. Chem.*, **20**, 673 (1948).

<sup>3</sup> Harvey, A. E., et al., *Anal. Chem.*, **25**, 498 (1953).

<sup>4</sup> Cheng, K. L., and Bray, R. H., *Soil Sci.*, **72**, 449 (1951).

<sup>5</sup> Cheng, K. L., *Chemist-Analyst*, **45**, 79 (1956).

<sup>6</sup> Hildebrand, G. P., and Reilly, C. N., *Anal. Chem.*, **29**, 258 (1957).

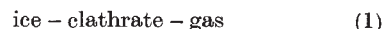
<sup>7</sup> Tucker, B., Ph.D. thesis, University of Illinois (1955).

<sup>8</sup> Arizona Agricultural Experiment Station Technical Paper No. 492.

### Validity of Clapeyron's Equation for Phase Equilibria involving Clathrates

CLATHRATES are solid solutions of a volatile solute in a host lattice<sup>1</sup>. The quinol clathrates studied by Powell<sup>2</sup> and the so-called gas hydrates<sup>3</sup> belong to this class of substances. Their host lattices, when empty, are thermodynamically unstable. In this respect they are different from the zeolites (Barrer<sup>4</sup>) in which the occluded component is sorbed in a stable host lattice. This has as a consequence that univariant phase equilibria involving a clathrate, in general, have no counterpart in the case of sorption in zeolites.

Consider, for example, a binary system water plus gas in which a clathrate (hydrate) occurs. The three-phase equilibria:



then are univariant ones in which the composition of the clathrate varies along the three-phase lines. The heat  $\Delta H$  of decomposition of the clathrate into ice and gas (1), or into solution and gas (2), can be found from the slope of the three-phase line and the change in volume  $\Delta V$ , according to Clapeyron's equation:

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} \quad (3)$$

The values of  $\Delta H$  per mole of solute thus obtained by earlier investigators and quoted by von Stackelberg<sup>5</sup> and Barrer and Stuart<sup>6</sup> are not invalidated by the fact that hydrates are solid solutions instead of stoichiometric compounds. Equation (3) is a direct consequence of the second law of thermodynamics, and as such exact for all univariant equilibria, irrespective of the number of components.

Quite separate from Clapeyron's equation, one has a relation which determines the change in composition of the clathrate solution necessary to maintain equilibrium with ice in (1), or with an aqueous liquid in (2), when temperature or pressure are varied (compare, for example, equation (3.12) of ref. 1a and equation (15) of ref. 5). The latter relation is completely analogous to the well-known formula for the depression of the freezing point of ideal liquid solutions.

Clearly, equilibrium (1) is not analogous to the sorption equilibrium of a gas in a zeolite. The latter is a bivalent equilibrium to which Clapeyron's equation is not applicable, and for which the heat of desorption is proportional to the derivative  $(\partial P/\partial T)$  at constant sorbed excess number of moles (cf. ref. 6, pp. 201-205, for an elegant treatment of this problem).

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<sup>3</sup> von Stackelberg, M., et al., *Naturwiss.*, **36**, 327, 359 (1949); *Z. Elektrochem.*, **58**, 25, 40, 99, 104, 162 (1954).

<sup>4</sup> Barrer, R. M., *Disc. Farad. Soc.*, **7**, 135 (1949). Dixième Conseil de Chimie, Institut International de Chimie Solvay, 21 (R. Stoops, Bruxelles, 1956).

<sup>5</sup> Barrer, R. M., and Stuart, W. I., *Proc. Roy. Soc., A*, **242**, 172 (1957).

<sup>6</sup> Guggenheim, E. A., "Thermodynamics", third edit., paras. 4.76-4.77 (North-Holland Pub. Co., Amsterdam, 1957).