

PRACTICAL METHODS IN PHASE RULE STUDY: TRANSITION TEMPERATURES FROM ELECTROMOTIVE FORCE MEASUREMENTS

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The methods available for the determination of transition temperatures have been classed by Findlay¹ under seven heads: (1) dilatometric methods, (2) vapor pressure methods, (3) solubility measurement methods, (4) latent heat measurement methods, (5) optical methods, (6) viscosimetric methods, and (7) electrical methods.

Any one of the above is subject to considerable refinement, and often great modification is necessary to make the method suitable. Of the methods listed above all but the last-named are open to the objection that the measurement depends upon a finite and appreciable change in quantity, from the metastable to the stable form. Only this one method appears to be applicable if

- (1) the transition temperature must be determined from solutions of the compounds, or
- (2) one of the compounds is indefinitely metastable.

Little mention of the applications of this method occurs in the literature.

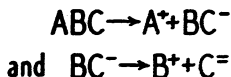
The method can be used only for electrovalent compounds, but, as will be shown in the sequel, it is of particular value in the case of complex salts of the Werner type which cannot be isolated from the mother liquor without decomposition.

Theoretical

A complete study of such a case would demand a knowledge of the extent of electrolytic dissociation of the complex itself, and of the complex ion which is formed. In the absence of such information, it might be assumed that the ion of greatest stability at a fixed temperature would produce fewer products of dissociation, hence the charge at its

electrode would be indicative of its stability. This is more clearly shown by an illustration.

Let the complex molecule ABC dissociate thus:



BC⁻ in this case being the complex ion, and let the metastable compound ADC dissociate in the same way



Two possibilities present themselves.

- A. The two instability constants are equal or approximately equal.
- B. They are not equal.

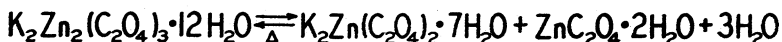
In the case that the instability constants of BC⁻ and DC⁻ are very nearly the same, the dissociation of the metastable ion will be enough greater to manifest itself as a positively charged electrode if metallic D is immersed in a solution of these ions.

In the second case, if the instability constants are considerably different, there will be only one condition when the dissociation of one species results in the same electromotive force as does the other. This is when the two complexes are at the transition temperature. In such a case the electromotive forces against the common metal are equal and the experimental manifestation of such condition is a zero electromotive force. The limiting condition which would make this method without value would be the practically impossible case where the two compounds give the same electrode potential, and have the same electromotive force-temperature coefficient.

With the above discussion in mind, the general case can now be made more specific using for example the complex oxalato-zincates. The author has recently demonstrated² that the complex salt $\text{K}_2\text{Zn}_2(\text{C}_2\text{O}_4)_3 \cdot x\text{H}_2\text{O}$ forms from concentrated potassium oxalate solutions which have been saturated with zinc oxalate at the boiling point, when one of these solutions is allowed to cool to room temperature.

Its metastable existence has been proved on the phase rule basis. This compound, on standing, spontaneously reverts to the stable complex, $K_2Zn(C_2O_4)_2 \cdot 7H_2O$.³ This reversion requires approximately three days for completion at room temperature but at more elevated temperatures the trioxalato-form can be kept over long periods of time (e. g. three months or more at 40°).

In order to define the phase rule isotherm for the trioxalato-complex under stable conditions it is, of course, necessary to determine the transition temperature for the reaction:

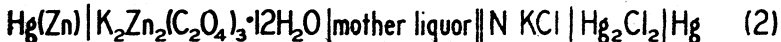


The various methods included in the list given in the introduction were all considered with regard to possibility and practicability and several were tried with uncertain results. Theoretically the electro-potential method should give the most dependable returns. In a recent series of measurements of an exploratory nature consistent data were obtained.

Experimental

For the purpose, two calomel electrode vessels were used and half-cells were built up in them, identical in every respect except in the complex salt added. These were connected in the customary manner through a salt bridge with a normal calomel electrode. The oxalate half-cells were kept in a thermostatic water bath regulated to $\pm 0.05^\circ C$. The calomel cell was kept in a thermostatic air bath at $20^\circ C$.

The system can be represented in the conventional way, thus:



where the oxalate electrode is negative and the calomel electrode positive. Potentials were measured by the null method with a voltmeter potentiometer which gave values uncertain in the fifth significant figure.

	T	E (volts)		T	E (volts)
For cell (1)	0°C	1.286	For cell (2)	0°C	1.262
	24	1.264		36	1.246
	72.5	1.226		56	1.240

Liquid junction potentials and temperature junction potentials are known to be negligibly small compared to the case at hand.

In the light of these preliminary data the transition temperature appears to be in the vicinity of 60°C. Further work is in progress with the purpose of refining the method and determining the temperature to a greater degree of precision.

There is evidence of a strong tendency toward polarization and to eliminate this possibility it will be necessary to use a vacuum tube voltmeter. Further data will be presented later.

BIBLIOGRAPHY

1. Findlay, Alexander, *The Phase Rule and Equilibrium*, New York, 1927.
2. Metler, V. (1934), "The System Zinc Oxalate, Potassium Oxalate, Water. II. At 35°", *Journal of the American Chemical Society*, Vol. 56, Pt. 2, pp. 1509-10.
3. Metler, V. and Vosburgh, Warren C. (1933), "The System Zinc Oxalate, Potassium Oxalate, Water. I. At 25°", *ibid.* Vol. 55, Pt. 2, pp. 2625-9.

THE FRANK CARNEY COLLECTION OF MAPS

Edwin J. Foscoe

The Department of Geology and Geography of Southern Methodist University has been fortunate in securing the entire collection of wall maps from the private library of the late Doctor Frank Carney¹ sometime Professor of Geology and Geography at Baylor University, Waco, Texas, and formerly of Denison University, Granville, Ohio.

Doctor Carney, who traveled widely, had made map collecting a hobby. Whenever he found a map that he wanted for his collection he secured it regardless of price. In that

¹See biographical sketch, "The Life and Works of Doctor Frank Carney" in *The Southwestern Social Science Quarterly*, Vol. 16, No. 3, pp. 51-59.