Thermochimica Acta, 34 (1979) 35—41

DETERMINATION OF THE LIQUID FRACTION PRESENT AT THE INITIAL TEMPERATURE OF SKAU'S TECHNIQUE OF CRYOMETRIC MEASUREMENT

ANDRZEJ BYLICKI and ZYGMUNT BUGAJEWSKI

Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warsaw (Poland)

(Received 16 January 1979)

ABSTRACT

A method has been described for evaluating the premolten liquid fraction (F_1) at a temperature adopted as the initial point in the melting curve ascertained by Skau's kinetic cryometry technique, based exclusively on the experimentally observed course of this curve.

INTRODUCTION

The quantity directly measured in Skau's kinetic cryometric technique is the varying temperature (T) of a substance sample examined as a function of time under programmed linear elevation of the surrounding temperature [1]. The progress in melting, followed in terms of the varying liquid fraction (F), is determined from the heat balance which involves the enthalpy of the solid—liquid phase transition and the heat capacity of the system and assumes the rate of heat transfer to be directly proportional to the differences of temperature between the sample and the surroundings.

Unlike the cryometric techniques which measure the liquid fraction by virtue of the differences in the properties between solid and liquid phases such as molar volume [2], dielectric constant [3] and nuclear magnetic resonance absorption [4], the Skau technique does not permit the direct measurement of the liquid fraction (F) existing in the system at an equilibrium temperature (T), nor worst of all does it allow the measurement of the liquid fraction (F_1) existing in the system at the initial experimental temperature (T_1). Only after the measurement has been completed can the heat balance evaluate, analytically or graphically, the variation in F value with the system temperature, provided that during the measurement F varies from 0 to 1.

Since Skau's melting curve is usually determined by starting with temperatures much higher than the freezing point of the polyeutectic formed by the major component (substance investigated) with minor (impurity) components, the system, at the initial experimental temperature adopted as the melting observation starts, already contains a certain amount, which is sometimes quite considerable, of the liquid phase whose proportion must be known if the kinetic melting curve is to be correctly interpreted.

Evaluation of the primary liquid fraction (F_l) present at the initial melting observation temperature, as a correction for incomplete crystallization, has not yet been satisfactorily described in the literature and is usually ignored in the cryometric analysis, thus sacrificing much of the accuracy of this method.

A general solution for this problem is not feasible if it is based only on the observation of the system temperature with no prior knowledge of either the impurity content or the type of solid—liquid equilibrium (SLE) existing between the major and the minor components. However, for well-defined phase equilibrium types, particular solutions are feasible. The study by Cisse et al. [5] may serve as an example. They have suggested a correction to account for incomplete crystallization, F_l at temperature T, based on the ideal solubility curve, viz.

$$F_l = \frac{(X_2^0/A)}{(X_2^0/A) + T_f - T} \qquad (1)$$

where T_f is the freezing temperature of the substance containing a mole fraction of X_2^0 impurities, and A is the first cryometric constant. This approach is inconvenient in that T_f is difficult to measure by Skau's technique, requiring extrapolation of the melting curve beyond the equilibrium range, and also in that, without prior knowledge of the (sought-for) correction (F_l), only an approximate value of X_2^0 can be found.

The present paper sets out to describe a way of evaluating the primary liquid fraction (F_l) at any equilibrium temperature (T) and thus at any point in the kinetic melting curve within the region where the phase transition can be assumed to proceed under equilibrium conditions. As demonstrated previously [6], this holds true only for the temperature range below the temperature of the inflection point in Skau's melting curve. The results obtained by the method suggested are not affected by the accuracy of measurement of absolute temperature in the melting curves, because they are evaluated from observed temperature differences and hence systematic temperature measurement errors, unavoidable with thermocouples, are cancelled out.

THEORETICAL

The Skau kinetic technique assumes that the increment in the surface area S (Fig. 1) bounded by the melting curve and by the surrounding temperature increase curve, with suitable corrections duly allowed for (inter alia, for the heat of warming of the system, heat losses, etc.) [7,5], corresponds to the heat effect of the solid—liquid transition and is directly related to the liquid fraction F. Thus the evaluation of the correction (F_l) for incomplete crystallization reduces to determining the surface area (S_l) corresponding to the heat of the phase transition over the temperature range extending from the actual commencement of melting, i.e. from the lowest temperature at which the liquid phase appears in a given system, up to the experimental temperature T_l which is taken as the start of observable melting in the cryometric measurement.

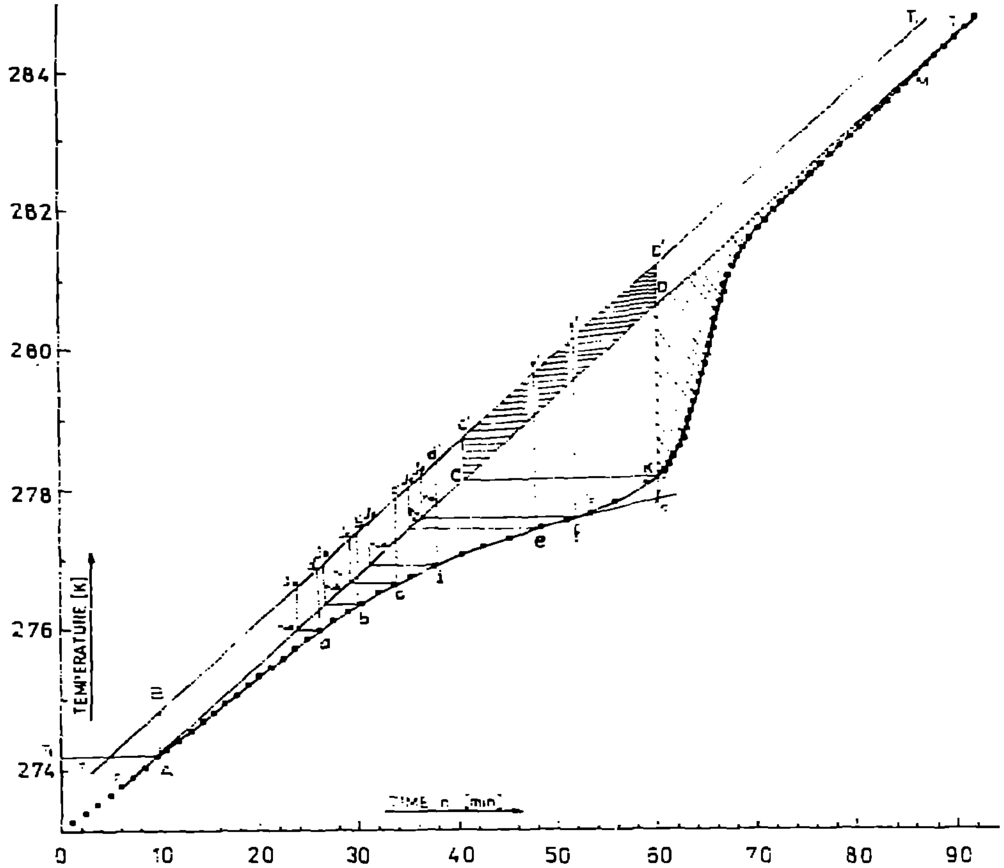

Fig. 1. The observed melting curve for the benzene sample to which 0.48 mole % of *n*-heptane was added.

If the total surface area assumed to represent the heat of the solid—liquid transition of a sample studied from the initial experimental temperature (T_1) to the end of the melting process is designated by S_c, then the correction for the liquid fraction existing at T_1 may be expressed as

$$F_1 = \frac{S_1}{S_1 + S_c} \tag{2a}$$

With ideal eutectics, in the diluted solution region at an arbitrarily chosen point *i* in the melting curve, the relation between the equilibrium temperature (T) and the corresponding liquid fraction melted (F) is

$$T_i = T_{fo} - \frac{X_2^0}{A}\frac{1}{F_i} \tag{3}$$

where T_{fo} is the freezing point of the 100% pure substance.

By writing the cryometric equation (eqn. 3) at three data points (i.e. at three experimental temperatures and corresponding surface mole fractions), viz. (T_1, F_1), (T_2, F_2), (T_3, F_3) and taking, in accordance with the assumptions underlying the Skau method, the fraction F_1 as given by eqn. (2a) and F_2 and F_3 as

$$F_2 = \frac{S_1 + S_2}{S_1 + S_c} \tag{2b}$$

$$F_3 = \frac{S_1 + S_3}{S_1 + S_c} \tag{2c}$$

and solving eqns. (2a)—(2c) and the respective eqn. (3) for S_1, we obtain

$$S_1 = \frac{(T_3 - T_2)S_2S_3}{(T_2 - T_1)S_3 - (T_3 - T_1)S_2} \tag{4}$$

For T_2 and T_3 we may take any two temperatures within the equilibrium melting region, between the temperature T_1 and the inflection point on the melting curve.

Evaluation of S_1 may also involve other forms of the solubility equation and corresponding cryometric equations. For example, if the freezing entropy, rather than the freezing enthalpy, is assumed to be independent of temperature, as adopted by Malesinski for a series of ideal eutectics [8,9], the resulting solubility equation is

$$-\ln X_1 = \frac{\Delta S_{m_1}}{R} (\ln T_{f_0} - \ln T) \tag{5}$$

and the corresponding cryometric equation [10] is

$$\ln T = \ln T_{f_0} - \frac{X_2^0}{k} \frac{1}{F} \tag{6}$$

where $k = \Delta S_{m_1}/R$.

Then, by proceeding as before, we arrive at eqn. (7) in place of eqn. (4), viz.

$$S_1 = \frac{(\ln T_3 - \ln T_2)S_2S_3}{(\ln T_2 - \ln T_1)S_3 - (\ln T_3 - \ln T_1)S_2} \tag{7}$$

In either of eqns. (3) or (6) the simplification $\ln X_1 = \ln(1 - X_2) \sim -X_2$ was used, a common assumption in the cryometry of diluted solutions, which holds true in regions of extreme dilution.

Rearrangement of Malesinski's solubility equation in the form $X_1 = (T/T_{f_0})^k$ renders this simplification redundant. Putting $X_1 = 1 - X_2$ gives

$$T^k = T_{f_0}^k - T_{f_0}^k X_2^0 \frac{1}{F} \tag{8}$$

and hence

$$S_1 = \frac{(T_3^k - T_2^k)S_2S_3}{(T_2^k - T_1^k)S_3 - (T_3^k - T_1^k)S_2} \tag{9}$$

EXPERIMENTAL

The application of the proposed method of evaluation of the correction (F_l) for incomplete crystallization is illustrated by a cryometric measurement carried out with a contaminated *n*-heptane sample of well-known composition. Benzene and *n*-heptane form a eutectic system, close to the ideal, with the eutectic temperature $T_E = -91.275°$C. Therefore, to determine the melting curve just from the appearance of the liquid phase would require starting the measurement at a temperature below 181.875 K (T_E). However, the cryometric measurement undertaken to determine the degree of purity of benzene by Skau's technique is usually carried out within a much narrower temperature range, especially since, if the impurities are unidentified, the lowest temperature of liquid phase appearance remains unknown.

The substances used (99.989 mole % pure benzene and 99.6 mole % pure *n*-heptane), the apparatus and the procedure were the same as described in the preceding paper [6].

A benzene sample to which 0.48 mole % of *n*-heptane was added was used for measurements.

The observed melting curve AKM (temperature vs. time) and the geometrical constructions used to ascertain the corrected surrounding temperature line T_j and to evaluate corrections 1 and 2 (refs. 5 and 7) are presented in Fig. 1.

RESULTS AND DISCUSSION

Equations (4), (7) and (9) were used to evaluate the liquid fraction F_1 at the observed initial melting temperature T_1. To check how the values S_1 and F_1 are affected by the points T_2 and T_3 arbitrarily chosen in the equilibrium region, calculations were performed for two different T_3 values (points e and f in Fig. 1) taken beneath the inflection point (I_p) and four T_2 values (points a, b, c, d) chosen within the range T_1 to T_3, i.e. for eight temperatures and corresponding surfaces (area sets) S_2 and S_3.

The calculations of surfaces S_2 and S_3 as well as of the total surface area S_c were carried out individually by two methods, viz. one involving correction 1 (Lyashkevich [7]) which adopts the line T_j in place of T over the whole phase transition region BD′ (total area, S_c = AFD′BA; area corresponding to any point, e.g. e, in the melting curve, S_e = Aee′BA), and the other involving in addition correction 2 (Cisse et al. [5]) for the heat of warming of the sample (total area S_c = AFD′C′CA; S_e = Aee′$J_e N_e$A).

Results are listed in Table 1. The total areas S_c are expressed in mm^2 as evaluated from a plot based on the experimental melting curve. The areas S_3 and S_2 obtained for each set of temperatures T_3 and T_2 and the area S_1 calculated from eqns. (4), (6) and (9) are expressed as percentages of S_c. The corresponding F_1 values were calculated from eqn. (2a).

It is worth noting that, if the liquid mole fraction present at the initial moment of observation of the melting curve is ignored, the use of correction 2 (ref. 5) may lead to greater errors in the results (as evident from Fig. 2 in ref. 6).

TABLE 1

Corrections for the liquid phase present at temperature T_1 adopted as the initial point in the Skau melting curve

Data for experimental melting curve (Fig. 1) of 99.52 mole % benzene containing 0.48 mole % of *n*-heptane; T_1 = 274.186 K.

Series I. Correction 1 applied; total area S_c = 14,975 mm^2.

No	T_3(K)	T_2(K)	S_3 (% of S_c)	S_2 (% of S_c)	S_1 (% of S_c)			F_1 (mole %)		
					from eqn.			for S_1 from eqn.		
					(4)	(6)	(9)	(4)	(6)	(9)
1	277.399	a 275.974	57.12	15.79	22.51	24.80	25.69	18.37	19.87	20.44
2		b 276.337		20.80	25.00	22.38	23.11	20.00	18.27	18.77
3		c 276.673		26.54	19.38	19.22	19.88	16.24	16.12	16.59
4		d 276.948		33.38	17.02	16.94	17.45	14.55	14.49	14.86
5	277.581	a 275.974	69.50	15.79	22.78	24.70	25.63	18.56	19.80	20.40
6		b 276.337		20.80	24.95	22.60	23.39	19.97	18.42	18.96
7		c 276.673		26.54	20.23	20.02	20.76	16.83	16.70	17.19
8		d 276.948		33.38	18.66	18.49	19.14	15.73	15.60	16.07

Series II. Corrections 1 and 2 applied; total area S_c = 11,500 mm^2.

No	T_3(K)	T_2(K)	S_3 (% of S_c)	S_2 (% of S_c)	S_1 (% of S_c)			F_1 (mole %)		
					from eqn.			for S_1 from eqn.		
					(4)	(6)	(9)	(4)	(6)	(9)
1	277.399	a 275.974	48.30	5.95	6.09	6.05	6.22	5.74	5.71	5.86
2		b 276.337		9.30	6.47	6.41	6.58	6.08	6.03	6.18
3		c 276.673		14.43	6.86	6.81	7.01	6.42	6.38	6.55
4		d 276.948		21.26	7.11	7.08	7.27	6.64	6.61	6.77
5	277.581	a 275.974	59.30	5.95	6.61	6.59	6.76	6.20	6.15	6.33
6		b 276.337		9.30	7.15	7.10	7.31	6.67	6.63	6.81
7		c 276.673		14.43	7.89	7.82	8.07	7.31	7.25	7.46
8		d 276.948		21.26	8.71	8.64	8.91	8.01	7.95	8.18

Incorrectly introducing the surface area into the initial area in the melting curve by extrapolating the T_j line according to correction 1 (ref. 5) compensates to a certain extent for the missing surface area caused by ignoring the thermal effect associated with partial melting of the sample before the measurement has been started. It is, therefore, compensation of the two errors that may explain the apparently striking effect that, especially with samples containing larger amounts of impurities, neglecting correction 2 leads to better results.

The results presented in Table 1 show that it is reasonable to choose a point in the melting curve for the determination of T_3 and S_3 close to the inflection point, a point for evaluation of T_2 and S_2 approximately in the middle of T_1 and T_3, correction 2 suggested by Cisse et al. [5] for the calculation of surface areas S_2 and S_3, and eqn. (9) for the evaluation of F_1, i.e. the equation derived from that of the cryometric curve in which the effect of the simplifying assumptions, viz. the adoption of a temperature-independent enthalpy of melting and of X_2 in place of $-\ln X_1$, was suppressed.

REFERENCES

1 E.L. Skau, Proc. Am. Acad. Arts Sci., 67 (1932) 551.
2 W. Świętosławski, J. Phys. Chem., 47 (1943) 590.
3 G.S. Ross and L.J. Frolen, J. Res. Natl. Bur. Stand., Sect. A, 67 (1963) 607.
4 L.J. Burnett and B.H. Muller, Nature (London), 219 (1968) 59.
5 Z. Cisse, P. Clechet, M. Coten, J. Delafontaine and H. Tachoire, Thermochim. Acta, 2 (1971) 357.
6 Z. Bugajewski and A. Bylicki, Thermochim. Acta, 27 (1978) 329.
7 N.T. Lyashkevich, Neftekhimiya, (in Russian) 1 (1961) 286.
8 W. Malesiński, Rocz. Chem., 30 (1956) 901.
9 W. Malesiński, Bull. Acad. Pol. Sci. Cl. 3, 3 (1955) 51, 267.
10 A. Bylicki and R. Lewandowska, Bull. Acad. Pol. Sci., Ser. Sci. Chim., 26 (1978) 557.