

## DIFFERENTIAL HEATS OF DISSOLUTION IN THE POTASSIUM BICHROMATE-WATER SYSTEM AT 25°C

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Received October 25th, 1977

Differential heats of dissolution in the potassium bichromate-water system were measured in the range of molal concentrations 0.065–0.491 *m* at 25°C. The dependence of the heat of dissolution on the concentration was expressed as  $L$  (kJ/mol) = 76.9368 – 43.5608  $\sqrt{m}$  + 27.6798*m*. The measured values were compared with published data and their consistency with measured integral values was discussed.

The integral heats of dissolution of potassium bichromate in water at 25°C published hitherto and measured by us in the wide concentration range 0.0009–0.498*m* were summarized in our preceding work<sup>1</sup>. Their direct measurement was carried out only by Perreu<sup>2,3</sup>, however his data are not consistent with the integral heats given by him<sup>2</sup>, which differ significantly from our<sup>1</sup> and other data for the integral heats of dissolution<sup>3</sup>.

The purpose of the present work was to measure the differential heats of dissolution of potassium bichromate in a wide concentration range on two calorimeters and to compare the results with Perreu's data<sup>2</sup> and with the differential heats calculated from the integral ones.

### EXPERIMENTAL

Potassium bichromate of reagent grade (Lachema) was triply recrystallized under stirring, dried at 80°C in an oven and then in an exsiccator with P<sub>2</sub>O<sub>5</sub> for several weeks at 25°C. Water was redistilled from a quartz apparatus<sup>4</sup>. The heats were measured in an LKB calorimeter of the type 8700–1 with 100 cm<sup>3</sup> reaction cells, and besides a Calvet-Standard microcalorimeter (Setaram, France, 200°C) with reaction cells 17 mm in diameter and a signal output to an ITC integration unit. Both instruments were calibrated with the reaction heat of tris(hydroxymethyl)-aminomethane<sup>5</sup> (NBS reference standard material No 724a) with 0.1*M*-HCl. The reaction cells of the firm Setaram were modified so that the dissolved substance, weighed in a mesh, could be transferred into the solvent. The more concentrated solutions were not stirred with respect to the high sensitivity of the measurement. The experimental conditions in measuring the differential heats were chosen so that the concentration changes were negligible, *i.e.*, they were equal to 0.002*m* in diluted and 0.003*m* in concentrated solutions. These concentration changes

correspond to a heat change of 0.114 and 0.010 kJ/mol representing a deviation from the measured values of about 0.1% for dilute and about 0.01% for concentrated solutions. These deviations are negligible against the experimental errors in measuring the differential heats. The temperature of measurement was  $25 \pm 0.01^\circ\text{C}$ .

## RESULTS AND DISCUSSION

The measured values of the differential heat of dissolution,  $L_E$ , on both calorimeters are given in Table I in the range of molalities from 0.065 to 0.491*m*. The table contains the initial and final molal concentrations, the square root of the mean molal concentration  $\bar{m}$ , from which the values of  $L_C$  were calculated with the use of Eq. (1) and further the relative errors in percent with respect to the experimental values,  $L_E$ .

The differential heat of dissolution as a function of the concentration was fitted by the following polynomial:

$$L_C(\text{kJ/mol}) = 76.9368 - 43.5608 \sqrt{m} + 27.6798m, \quad (1)$$

whose chosen degree was not so critical as in the case of the concentration dependence of the integral heats of dissolution<sup>1</sup>. In Table I are given the relative deviations,  $\varepsilon$ , of the measured values,  $L_E$ , from the calculated ones,  $L_C$ , from Eq. (1) found by the least squares method. Our values of the differential heat differ from those found by Perreu<sup>2</sup> on the average by less than 1% as is apparent from Fig. 1.

The extrapolated value of the differential heat of dissolution at saturation, *i.e.*, the value of the last heat of dissolution,  $L_s$ , is equal to  $59.95 \pm 0.9$  kJ/mol (with respect to the literature data<sup>3</sup>, we considered a 0.511*m* solution as saturated at  $25^\circ\text{C}$  assuming the molar mass of  $\text{K}_2\text{Cr}_2\text{O}_7$  equal to 294.192). This value is in a very good agreement with the value of  $59.9 \pm 0.9$  kJ/mol obtained by extrapolation of Perreu's

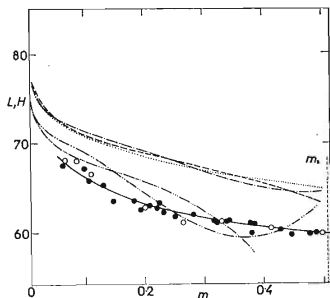


FIG. 1

Differential,  $L$  (kJ/mol), and Integral Heats of Dissolution,  $H$  (kJ/mol), in the  $\text{K}_2\text{Cr}_2\text{O}_7$ - $\text{H}_2\text{O}$  System at  $25^\circ\text{C}$  as Functions of Molality,  $m$  (mol/kg)

● This work; ○ Perreu<sup>2</sup>; ———  $L_C$  according to Eq. (1); - - - - - and - · - · - differential heats calculated from measured values of  $H$  fitted by polynomials of the third and fourth order<sup>1</sup>; - - - and - · - · - measured values of  $H$  approximated by polynomials of the third and fourth order<sup>1</sup>; · · · · · values of  $H$  calculated from measured  $L_E$  approximated by Eq. (1) with the use of (3b).

differential data<sup>2</sup> (Eq. (10) in ref.<sup>1</sup>) and with the value of the heat of crystallization,  $-60.04$  kJ/mol, measured by him<sup>2,3</sup>. There is also a surprising agreement with the data of Shmagin and Shidlovskii<sup>6</sup>, whose interpolated value for the saturation region lies in the intersection of the dependences approximating our and Perreu's data.

The concentration dependence of the differential heat of dissolution can be obtained also from the measured integral heat of dissolution with the use of the following

TABLE I  
Measured Differential Heats of Dissolution,  $L_E$  (kJ/mol), of  $K_2Cr_2O_7$  in Water at 25°C

$m$ initial mol/kg	$m$ final mol/kg	$\bar{m}^{1/2}$	$L_E$ kJ/mol	$\delta$	$\varepsilon^a, \%$	Calorimeter
0.065	0.067	0.257	67.500	-0.073	-0.11	LKB
0.100	0.102	0.318	67.090	1.201	1.79	LKB
0.108	0.110	0.330	65.736	0.164	0.25	LKB
0.133	0.135	0.366	65.263	0.563	0.86	LKB
0.138	0.139	0.372	62.400	-2.159	-3.46	Calvet
0.151	0.152	0.389	63.583	-0.592	-0.93	LKB
0.186	0.188	0.432	63.533	0.257	0.40	LKB
0.196	0.198	0.444	62.664	-0.391	-0.62	LKB
0.209	0.210	0.458	62.975	0.178	0.28	LKB
0.225	0.227	0.475	62.805	0.321	0.51	LKB
0.228	0.230	0.479	63.391	0.961	1.52	LKB
0.236	0.238	0.487	62.342	0.052	0.08	LKB
0.254	0.256	0.505	61.865	-0.133	-0.22	LKB
0.287	0.289	0.537	61.990	0.459	0.74	LKB
0.320	0.322	0.567	61.463	0.321	0.52	LKB
0.324	0.325	0.570	61.224	0.119	0.20	LKB
0.334	0.336	0.579	59.664	-1.333	-2.23	Calvet
0.339	0.340	0.583	61.191	0.238	0.39	LKB
0.344	0.346	0.587	61.475	0.575	0.94	LKB
0.380	0.382	0.617	61.100	0.505	0.83	Calvet
0.384	0.386	0.620	60.071	-0.494	-0.82	LKB
0.387	0.389	0.623	61.123	0.573	0.95	LKB
0.391	0.395	0.627	59.304	-1.203	-2.03	Calvet
0.432	0.433	0.658	60.472	0.211	0.35	LKB
0.448	0.451	0.670	59.870	-0.304	-0.51	Calvet
0.477	0.480	0.692	60.086	0.037	0.06	Calvet
0.488	0.491	0.700	60.250	0.241	0.40	Calvet

$$^a \varepsilon = [(L)_E - (L)_C]/(L)_E = \delta/(L)_E.$$

equation:

$$L = H + m \partial H / \partial m. \quad (2)$$

Conversely, the differential values can be transformed to the integral ones by using the equations

$$H = (m_s/m) H(m_s) + m^{-1} \int_m^{m_s} L(m) dm \quad (3a)$$

or

$$H = - \int_0^m L(m) dm/m, \quad (3b)$$

where  $L$  and  $H$  are the differential and integral heats of dissolution,  $m_s$  denotes molality of the saturated solution. By these equations, the values of  $L$  and  $H$  obtained experimentally can be compared, their consistency objectively judged, and the suitability of the mentioned methods can be verified especially with regard to the differential heat of dissolution at saturation.

The measurement of the integral heats is simpler than of the differential ones since they are much larger, the experimental setup is simpler and the reproducibility of the results is much better. In our case the attained accuracy was  $\pm 1\%$ , whereas the differential heats were obtained with an accuracy of  $\pm 2\%$ . Therefore, most authors prefer to measure the integral heats of dissolution or dilution; a detailed analysis of the calculation of the differential heat of dissolution at saturation based on the measured integral or differential heats is missing.

The calculation of the integral from the differential heats according to Eq. (3b) assumes the knowledge of the concentration dependence  $L(m)$  in the diluted concentration region. This requires the measurement of small heats with a maximum accuracy, a larger ensemble of measured data being preferable for optimum results. If this dependence is known for a suitably chosen concentration region, the local error in the value of  $L(m)$  is manifested in the calculated value of  $H$  only in the ratio of the corresponding integrals.

The calculation of the differential heats from the measured integral dissolution heats according to Eq. (2) is simple, however the obtained values are much influenced not only by the error in the value of  $H$  but also by the induced error in the value of  $\partial H / \partial m$ , since the differential heat is determined solely by the course of the function  $H(m)$  in the point considered. Therefore, when the measured integral heat of dissolution<sup>1</sup>, accurate to within about 1%, is used to calculate the differential heat  $L(m)$ , the error of the results<sup>1</sup> increases up to 7%. Especially the extrapolation of the differential heat thus calculated to the saturated concentration is very inaccurate; a more accurate determination of the  $L(m)$  value at saturation is difficult<sup>1</sup>.

To evaluate the consistency of both kinds of data, it is therefore preferable to compare the concentration dependences of the heats of dissolution in the differential form. The mutual relations of the directly measured and recalculated integral and differential heats of dissolution are illustrated in Fig. 1.

If we compare the consistency of the integral and differential heats of dissolution measured by us, considering only such experimental values that differ from the regression function by not more than 2%, then the inconsistency of our data remains within the limits of the expected experimental error, *i.e.*,  $\pm 1$  and  $\pm 2\%$  for the measurement of integral and differential heats, respectively. Perreu's values of the integral and differential heats of dissolution are mutually inconsistent. Since our measured differential heats are in a good agreement with Perreu's data<sup>2</sup>, whereas the integral heats are at variance<sup>1</sup>, we suppose that his integral heats of dissolution of potassium bichromate are subject to an error of 4–5% due probably to an imperfect drying of the salt.

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Translated by K. Míčka.