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Test measurements and analysis of errors for a new equipment for the determination of excess-heat data

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Abstract

In this paper the systematic application of error analysis, error propagation and sensitivity calculations for the improvement of a calorimeter is shown. Adaptions were made on a SETARAM C-80 heat flux calorimeter to perform measurements of excess-heat data above the boiling point of the components. Test measurements were performed for the system n-hexane - c-hexane at 25, 40, 60 and 80 °C and for glycerol - water at 50 and 70 °C. The analysis of these results, error and sensitivity calculations show the sources of error and permit improvement and tuning of the equipment, which is demonstrated by improved results.

1. INTRODUCTION

Caloric measurements for chemical engineering applications require broad ranges of temperatures and pressures for a wide variety of substances. A SETARAM C-80 heat flux calorimeter indicates limitations in this respect concerning the measurement of heat of mixing data of liquids. So the mixing cells are restricted to atmospheric pressures and vaporization effects may cause considerable errors. To enable measurements of systems with low boiling components in the temperature range 20 - 120 °C and at pressures up to 25 bar adaptions of the equipment had to be made.

This paper deals with the presentation of test measurements and the analysis of their results. Applied error analysis and sensitivity calculations serve to find out the sources of errors and their influence on the results, this permits effective improvement and tuning of the equipment.

2. EXPERIMENTAL EQUIPMENT AND EVALUATION OF MEASUREMENTS

Apparatus, measurement and evaluation are described here

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only as necessary for error considerations and error calculations. A more detailed description will be given elsewhere [1].

Experimental equipment

The SETARAM C-80 is a heat flux calorimeter designed according to Calvet [2,3]. Two cells in a thermostat are thermally connected to this by about 200 regularly arranged thermocouples in series. A heat effect in one cell causes a temperature gradient and thereby a heat flux from the cell to the surroundings or vice versa through the thermocouples. This heat flux is quantitatively indicated by a thermovoltage. Its integral over time is proportional to the heat effect in the cell. The twin principle, connecting the two thermopiles in opposition, warrants high stability of the baseline against small changes of the thermostat temperature.

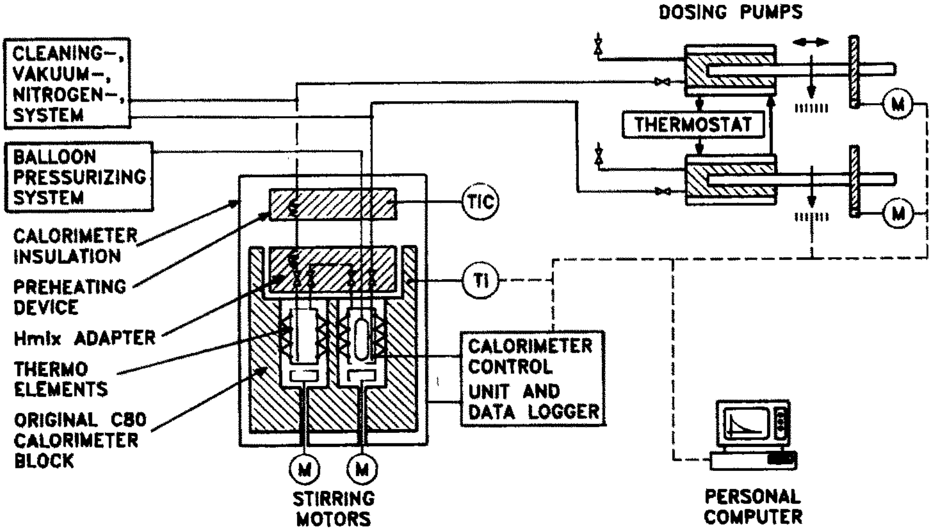

Figure 1. Apparatus block diagram

To allow measurements of components above the atmospheric boiling point and to avoid vaporization effects adaptions of the instrument were made in following respects:

- A SWAGELOCK piping system was installed to perform handling and mixing of the components.

- Pumping and metering of the components are effected by thermostated piston injectors, constructed in a manner similar as suggested by Gaube and Spiske [4], measuring the stroke of an exactly manufactured piston with high precision.

- Vapor phase in the measuring cell and vaporization effects are avoided by balloons made of VITON, pressurized with nitrogen.

Due to local temperature gradients within the thermostat an additional preheating device had to be constructed to warrant identical temperatures of the components before mixing.

A block diagram of the apparatus is shown in Figure 1. Details of the equipment, the data acquisition system etc. are given elsewhere [1].

Evaluation of measurements

The VITON balloon permits a variation of the mixture volume in the measuring cell from 1.5 to 8 ml. For each measurement about 7 ml of the components in sum are injected, their amounts defined by the desired composition are calculated by equation (1):

$$V_i = a_i \cdot l_i \ , \qquad i = \text{component } 1,2 \ , \qquad (1)$$

where a_i is the cross-section area of the according piston and l_i the piston stroke. Molecular weight M_i and density ρ_i permit the determination of the injected molar amount n_i:

$$n_i = V_i \cdot \rho_i / M_i \ . \qquad (2)$$

The thermovoltage of the baseline E_0 is measured before and after each experiment. The actual thermovoltage is protocolled by the data logger with a period of 5 seconds. The calculation of the experimental heat of mixing h_{exp}^E follows equation (3):

$$h_{exp}^E = A \cdot S / (n_1 + n_2) \ , \qquad (3)$$

where

$$A = \int_{t=0}^{t} (E - E_0)\, dt \ , \qquad (4)$$

t is the measuring time and S the sensitivity factor determined by calibration with a Joule cell and c_p-measurements of synthetic sapphires. The integration is performed numerically.

The molar excess heat data h_{exp}^{E} ($J\ mol^{-1}$) of each isothermal series are subjected to a Redlich-Kister (RK) expansion (5):

$$h_{calc}^{E} = x_1\ x_2 \sum_{i=1}^{n} A_i\ (2x_1 - 1)^{i-1}\ . \qquad (5)$$

The number of parameters A_i is defined to give the best fit of the experimental values with the minimum possible number of parameters. The root mean squared deviation (RMSD), defined by equation (6) may serve as a measure for the random errors of the experiments [7]:

$$RMSD = \sqrt{\sum_{j} (h_{exp}^{E} - h_{calc}^{E})_j^{2}\ /\ M}\ ,\quad j = 1, \ldots M\ , \qquad (6)$$

M is the number of measured points of each series.

3. RESULTS OF TEST-MEASUREMENTS

Test measurements were performed to check the accuracy and the limits of applicability of the equipment. The system n-hexane - c-hexane was chosen, since it is a calorimetric test system and reference data of high precision at 25 °C are given in the literature. Furthermore experiments at elevated temperatures allow to prove measurements above the atmospheric boiling point.

Glycerol - water was chosen as second test system. Although no reference data exist, its high viscosity was expected to show limits and possible problems with the equipment.

n-hexane - c-hexane

Measurements were performed at 25, 40, 60 and 80 °C. The n-hexane was a Fluka reagent (No. 52766, > 99.5 moles percent), c-hexane a Merck reagent (No. 2817, > 99.7 moles per cent). Both were carefully degassed and sucked into sample cylinders to be connected with the pumps directly by quick-connections.

The results of the measurements at 25 °C [6] are shown in Table 1. A Redlich-Kister expansion with 5 parameters correlates the measured values with a RMSD of 3.9 J/mol, corresponding to 2.3 % of the mean of all measured values. For comparison reference data of Marsh [8], calculated for the same compositions with a 6 parameter Redlich-Kister expansion are listed. Marsh's own data show a RMSD of 0.09 J/mol for the parameters A_1 = 864.6, A_2 = -246.73, A_3 = 98.092, A_4 = -42.021, A_5 = 3.8451, A_6 = 7.7786. The RMSD of our measurements from the RK-expansion of Marsh is 5.23

J/mol, corresponding to 3.0 % of the mean of the measured values. The mean deviation of our data from the reference values is -0.9 J/mol. δh_{exp}^E is the deviation of the measured values from the RK-expansion of our values, δh_{ref}^E the deviation of our measurements from the reference data of Marsh.

Table 1
h^E of n-hexane (1) - c-hexane (2) at 25 °C: measurements, reference data and deviations

x_1	h_{exp}^E J/mol	h_{calc}^E J/mol	δh_{exp}^E J/mol	h_{ref}^E J/mol	δh_{ref}^E J/mol
0.12	110.	110.93	-0.93	118.96	-8.96
0.25	185.	182.91	2.09	190.83	-5.83
0.34	209.	210.53	-1.53	214.30	-5.30
0.45	221.	221.38	-0.38	220.35	0.65
0.47	226.	220.73	5.27	219.15	6.85
0.49	215.	219.29	-4.29	217.31	-2.31
0.52	210.	215.71	-5.71	213.38	-3.38
0.53	217.	214.14	2.86	211.77	5.23
0.61	200.	195.42	4.58	193.80	6.20
0.66	175.	178.7	-3.73	178.26	-3.26
0.73	155.	150.19	4.81	151.39	3.61
0.79	123.	121.97	1.03	123.97	0.97
0.82	100.	106.81	-6.81	108.83	-8.83
0.92	55.	51.59	3.41	52.02	2.98

Redlich-Kister-parameters:
A_1 = 873.133 A_2 = -220.311 A_3 = -70.811 A_4 = -10.343
A_5 = 138.565 RMSD = 3.9 J/mol

Table 2 shows the results at 40 °C. Since no reliable reference data are available in the literature [7] for this temperature, an interpolation of the measurements of Ewing and Marsh [9] at 15 and 45 °C was made for comparison. A RK-expansion correlates our values with an RMSD of 2.2 J/mol, corresponding to 1.3 % of the mean of the measured values. The RMSD of our measurements from the RK-expansion of Ewing and Marsh is 6.5 J/mol, corresponding to 3.9 % of the mean of measured values. The mean deviation of our data from the values of Marsh is +3.1 J/mol.

Table 2
h^E of n-hexane (1) - c-hexane (2) at 40 °C: measurements, reference data and deviations

x_1	h_{exp}^E J/mol	h_{calc}^E J/mol	δh_{exp} J/mol	h_{ref}^E J/mol	δh_{ref}^E J/mol
0.15	132.	131.36	0.64	126.01	5.99
0.20	152.	153.74	-1.74	152.05	-0.05
0.29	184.	181.99	2.01	183.27	0.73
0.40	201.	201.18	-0.18	198.73	2.27
0.50	198.	202.65	-4.65	195.04	2.96
0.55	200.	196.52	3.48	187.77	12.23
0.57	193.	192.70	0.30	183.94	9.06
0.60	187.	185.47	1.53	177.26	9.74
0.65	170.	169.57	0.43	163.75	6.25
0.71	142.	144.74	-2.74	143.86	-1.86
0.80	100.	99.04	0.96	107.19	-7.19

Redlich-Kister-parameters:
A_1 = 810.608 A_2 = -148.564 A_3 = -135.930 A_4 = -378.715
A_5 = 218.213 RMSD = 2.2 J/mol

The results of the measurements at 60 and 80 °C are listed in Table 3 and Table 4. No reference values are available in the literature for these temperatures. At 60 °C a 3 parameter RK-expansion shows a RMSD of 5.2 J/mol corresponding to 3.5 % of the mean of all measured values. The measurements at 80 °C are correlated with a RMSD of 5.3 J/mol, corresponding to 4.7 % of the mean of all measured points.

Table 3
h^E of n-hexane (1) - c-hexane (2) at 60 °C: measurements and deviations

x_1	h_{exp}^E J/mol	h_{calc}^E J/mol	δh_{exp}^E J/mol
0.23	123.	123.10	-0.10
0.31	148.	152.00	-4.00
0.38	174.	168.67	5.33
0.48	177.	177.21	-0.21
0.58	170.	167.65	2.35
0.67	135.	144.84	-9.84
0.74	126.	119.37	6.63

Redlich-Kister-parameters:
A_1 = 706.894 A_2 = -85.074 A_3 = -197.943 RMSD = 5.2 J/mol

Table 4
h^E of n-hexane (1) - c-hexane (2) at 80 °C: measurements and deviations

x_1	h_{exp}^E J/mol	h_{calc}^E J/mol	δh_{exp}^E J/mol
0.15	92.	83.09	8.91
0.24	111.	121.51	-10.51
0.48	163.	159.90	3.10
0.49	160.	159.32	0.68
0.60	145.	142.29	2.71
0.60	143.	142.29	0.71
0.74	94.	97.67	-3.67
0.74	91.	97.67	-6.67
0.81	74.	69.74	4.26
0.81	72.	69.74	2.26

Redlich-Kister-parameters:
A_1 = 634.283 A_2 = -166.637 A_3 = -202.494 RMSD = 5.3 J/mol

Glycerol - water

Measurements were performed at 50 and 70 °C. Glycerol was a Fluka reagent (No. 49770,. water content < 0.1 %) and was used directly, all manipulations were done in a glove bag under dried nitrogen due to its hygroscopicity. Bidistilled demineralized water was degassed and filled into the sample cylinders.

While the measurements for n-hexane - c-hexane lasted about 5 000 seconds, the system glycerol - water showed extremely long duration of mixing up to 60 000 seconds. To enable measurements within a shorter period of time a special procedure for the evaluation of the heat-flux-curve was developed. The method is based on a fitting procedure of the descending branch of the curve permitting analytical integration of the tail. This procedure will be published elsewhere [1].

The results of the measurements at 50 and 70 °C are listed in Table 5 and Table 6. Again a 3-parameter RK-expansion was used for the correlation. They show a RMSD of 27.5 J/mol corresponding to 7.2 % of the mean measured values at 50 °C and 23.8 J/mole resp. 6.9 % at 70 °C.

Table 5
h^E of glycerol (1) - water (2) at 50 °C: measurements and deviations

x_1	h_{exp}^E J/mol	h_{calc}^E J/mol	δh_{exp}^E J/mol
0.23	-326.65	-320.15	-6.50
0.26	-360.59	-353.49	-7.10
0.37	-426.98	-453.75	26.77
0.62	-506.68	-518.51	11.83
0.75	-465.53	-438.03	-27.50
0.79	-399.08	-394.55	-4.53
0.79	-429.33	-394.55	-34.78
0.84	-334.35	-326.75	-7.60
0.89	-174.02	-243.22	69.20

Redlich-Kister-parameters:
A_1 = -2077.76 A_2 = -508.75 A_3 = -16.12 RMSD = 27.5 J/mol

Table 6
h^E of glycerol (1) - water (2) at 70 °C: measurements and deviations

x_1	h_{exp}^E J/mol	h_{calc}^E J/mol	δh_{exp}^E J/mol
0.26	-205.73	-208.34	2.61
0.41	-348.37	-346.88	-1.49
0.52	-424.95	-422.88	-2.07
0.71	-456.55	-422.22	-34.33
0.76	-334.33	-391.39	57.06
0.86	-296.61	-270.81	-25.80

Redlich-Kister-parameters:
A_1 = -1655.74 A_2 = -1075.21 A_3 = 344.12 RMSD = 23.8 J/mol

4. ANALYSIS OF ERRORS

The target of this chapter is to analyze the possible error sources and to quantify errors of primary measurements. Error propagation permits to calculate the influence of primary errors on the errors of measured values h_{exp}^E. These sensitivity calculations allow to prove quantitatively the completeness of the error analysis and furthermore to perform effective improvements and tuning of the equipment.

A general analysis of the test measurements shows high random errors. For n-hexane - c-hexane the RMSD increases with temperature and is about 5 % of the mean of all measured values for the measurements at 80 °C. The results of glycerol - water indicate mean errors of about 7 %. It should be noted that the biggest errors appear for high concentrations of glycerol.

Systematic errors

Although the results show high random errors, the correlation of data by the Redlich-Kister expansion permits a rough estimation of systematic errors.

This is primarily done by comparison with reference measurements. For n-hexane - c-hexane at 25 °C excellent measurements were published by Marsh [8]. Our data indicate a mean deviation of -0.9 J/mol from these values. The measurements at 40 °C may be compared with interpolated measurements of Ewing and Marsh [9] at 15 and 45 °C. The mean deviation of 3.1 J/mol of our data from these calculated reference values indicates a slight, but not statistically significant systematic error, considering the RMSD and the comparatively small number of measured points.

For all other series of measurements no reference data exist. Nevertheless the interrelation of temperature dependence of the h^E-data and excess heat capacity cp^E may be utilized for a rough estimation of the quality of the data.

Figure 2 shows a comparison of the evaluations of the measurements at 25 and 40 °C and of the measurements of Ewing and Marsh [9] with experimental cp^E of Ghassemi and Grolier [10].

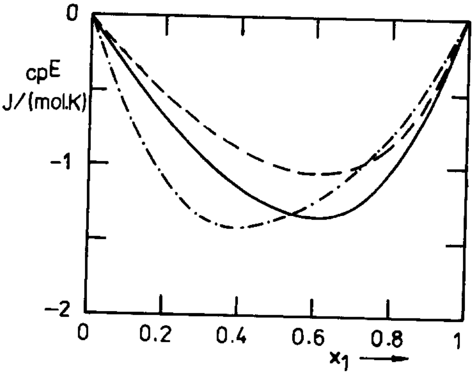

Figure 2: Measured and estimated cp^E of n-hexane - c-hexane at 25 °C. —— Measurements of Grolier, --- evaluation of our h^E-measurements, -·-·- evaluation of data of Ewing and Marsh

Evaluation of the Redlich-Kister expansions at 60 and 80 °C for n-hexane - c-hexane deliver similar results. The measurements of glycerol - water at 50 and 70 °C result in positive cp^E with a maximum of about 7.5 J/mol.

These evaluations confirm that there is no significant indication for large systematic errors.

Random errors

Basis for an analysis of errors is equation (3), indicating two sources of random errors: the **amounts n1, n2 [moles] of the components** mixed and the **integral of the heat flux curve A** [mVsec]. The sensitivity factor S, containing for simplicity here the step of amplification too, can only cause systematic errors.

The **amounts of components** are calculated by equations (1) and (2). Since the pumps are thermostated with an accuracy ± 0.1 K and the pump-pressure is controlled, density errors may be neglected and only volume errors may occur.

These metering errors ΔV may stem from inaccuracies of the measurement of the piston stroke, inexact manufacturing of the piston (diameter), compression of sealings etc. Experimental calibration of the pumps resulted in a mean error ΔV of ± 0.03 ml, the maximum error ΔV_{max} is about ± 0.06 ml.

According to equation (2) the molar amounts injected into the measuring cell depend on the metered volumes V_i and the specific properties density ρ_i and molecular weight M_i of the components. As mentioned above for all measurements the sum of the volumes of components mixed was about 7 ml. The differences of specific properties of the components of the different systems result in different interdependencies of volume ratios and mole fractions. For 7 ml total volume these interrelations may be derived from equation (2) resulting in equation (7) and (8):

$$V_1 = \frac{7\, x_1\rho_2/M_2}{x_1\rho_2/M_2 + (1-x_1)\,\rho_1/M_1}, \tag{7}$$

$$V_2 = \frac{7\,(1-x_1)\,\rho_1/M_1}{x_1\rho_2/M_2 + (1-x_1)\,\rho_1/M_1}. \tag{8}$$

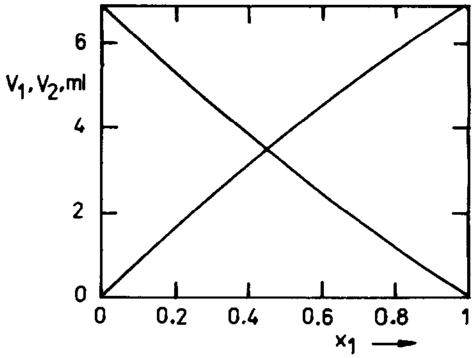

Figure 3: Interdependence between metered volumina of components and mole fraction for n-hexane (1) - c-hexane (2) at 25 °C

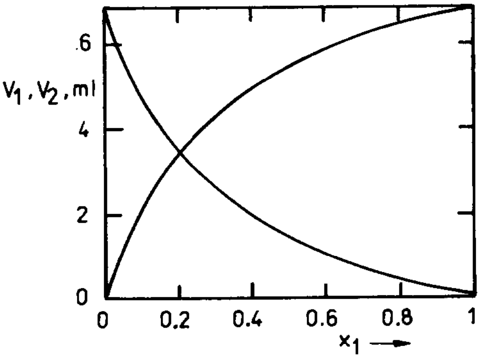

Figure 4: Interdependence between metered volumina of components and mole fraction for glycerol (1) - water (2) at 50 °C

Figure 3 demonstrates this interrelation for n-hexane - c-hexane, Figure 4 for glycerol - water. While the former system shows a nearly linear interdependence between V_i and x_i, the system glycerol - water indicates a high sensitivity of mole fraction against volume errors for concentrations of glycerol x > 0.5.

The **integral of the heat flux curve A** is given by equation (4), depending on time t, actual thermovoltage E(t) and the baseline voltage E_o.

Time measurement errors cannot cause random errors, as they are eliminated by the calibration, but the duration of measurement, especially long tailing, may cause considerable errors.

The analog-output of the amplifier (0 - 1.2 V) is digitalised by a 10-bit AD-converter of the data-logger. This results in an error of about ± 1.2 mV.

Concerning the actual thermovoltage E this error may be neglected since several thousand values are utilized for evaluation of each heat flux curve.

Concerning the baseline voltage E_O this inaccuracy can cause considerable random errors depending on the duration of the measurement. The measuring time for n-hexane - c-hexane was about 5000 seconds, delivering a value of the integral A of about 300 000 mVsec. An uncertainty of the baseline of 1.2 mV may cause integration errors of 2 % for this system. The system glycerol - water required a measuring time of 50000 seconds and gave a result for the area A of about 1 500 000 mVsec. The uncertainty of the baseline can cause errors of 4 %.

Although the errors of volume and baseline are of considerable magnitude, they can explain the large RMSD only in part as proved by sensitivity calculations. Another source of errors had to be detected therefore and finally this was found to be arbitrary fluctuations of the baseline. As mentioned above the baseline signal E_O was evaluated before and after each experiment indicating a small drift in some cases. A thorough examination with empty and full cells, making experiments with a durance of several days, showed irregular oscillations of E_O, their magnitude about 5 mV increased with temperature. High precision measurements of the thermostat's temperature indicated that these fluctuations of the baseline are associated with temperature changes of about 0.03 K. The reason was found to be the fluctuation of the voltage of the public current-network of about 5-10 %, disturbing the PID regulation of the thermostat. Constant power supply immediately effected a stable baseline as to be expected for Calvet-type heat-flux calorimeters. These problems have to be mentioned here because most producers of calorimeters give no specifications for power supply and in our case this circumstance may have effected maximum errors of the integral A up to 10 % for n-hexane - c-hexane and 20 % for glycerol - water.

Summarizing this rough analysis we may state two independent sources of random errors. **Volume metering errors ΔV** were determined by experiments. Their absolute size is ± 0.03 ml in mean and ± 0.06 ml in maximum for both components. Their effect on experimental results depends on the composition. **Integral errors ΔA** are caused by baseline inaccuracies and arbitrary baseline instabilities. Their magnitude depends on the system resp. the duration of measurement and is about 2-4 % for the former and up to 10-20 % for the latter cause in maximum. It is neither possible to give a mean value nor to separate these two causes in their effect on the error of h^E.

Error propagation and sensitivity calculations

The purpose of sensitivity calculations is to find out the influence of errors of primary measured data on the errors of experimental results. For this aim utilization of equation (3), used to evaluate h_{exp}^E from primary data, is not satisfying, since it does not include the composition as a variable. Therefore the attributed "true value", calculated from a Redlich-Kister-expansion of reference data, may be erroneous too due to composition errors. Basis for the calculation of error propagation is the deviation of measurements from reference data as given by equation (9):

$$\delta h^E = h_{exp}^E - h_{ref}^E \ . \qquad (9)$$

Substitution of equations (3) and (5) results in

$$\delta h^E = \frac{A \cdot S}{n_1 + n_2} - x_1 \ (1 - x_1) \ \sum_{i=1}^{n} A_{i,ref} \ (2 \ x_1 - 1)^{i-1} \ . \qquad (10)$$

Equation (10) describes the error of a measurement as function of the primary measured data taking into account equations (1), (2) and (4) and the definition of the mole fraction. Its values must be zero if all quantities are correct, h_{exp}^E being h_{ref}^E in this case.

Development of a Taylor-series at this point, cutting off after the first term, results in an equation (11) describing the deviation Δh^E as function of the deviation of the measured data from their correct values, that means their errors:

$$\Delta h^E = \left(\frac{\partial \delta h^E}{\partial V}\right) \Delta V + \left(\frac{\partial \delta h^E}{\partial A}\right) \Delta A \ . \qquad (11)$$

Application of error calculus results in

$$\Delta h_{mean}^E = \pm \sqrt{\left(\frac{\partial \delta h^E}{\partial V}\right)^2 \Delta V^2 + \left(\frac{\partial \delta h^E}{\partial A}\right)^2 \Delta A^2} \ , \qquad (12)$$

$$\Delta h_{max}^E = \pm \left[\sqrt{\left(\frac{\partial \delta h^E}{\partial V}\right)^2 \Delta V_{max}^2} + \sqrt{\left(\frac{\partial \delta h^E}{\partial A}\right) \Delta A_{max}^2} \ \right] , \qquad (13)$$

as general correlations between mean and maximum experimental errors and the errors of primary data. These equations are powerful tools for analysis of errors, since they permit to calculate the effect of primary errors on the results, but they may also serve to find out the completeness of an analysis of errors. In our case they brought up the random baseline instabilities analyzing the data of Miklautsch [6] presented in chapter 3.

It may easily be verified that performance of this derivation utilizing equations (1)-(10) results in equations (14) and (15):

$$\Delta h_{mean}^E = \pm\sqrt{(h_{ref}^E \frac{\Delta A}{A})^2 + (h_1^E \frac{x_1}{V_1} \Delta V)^2 + (h_2^E \frac{1-x_1}{V_2} \Delta V)^2}\ , \tag{14}$$

$$\Delta h_{max}^E = \pm\ [\sqrt{(h_{ref}^E \frac{\Delta A_{max}}{A})^2} + \sqrt{(h_1^E \frac{x_1}{V_1} \Delta V_{max})^2} + \sqrt{(h_2^E \frac{(1-x_1)}{V_2} \Delta V_{max})^2}\ ]\ . \tag{15}$$

h_1^E and h_2^E are the partial molar excess enthalpies to be derived from the Redlich-Kister expansion given by equations (16) and (17):

$$h_1^E = x_2^2\ [A_1 + A_2\ (3x_1 - x_2) + A_3\ (5x_1 - x_2)\ (x_1 - x_2) + A_4\ (7x_1 - x_2)\ (x_1 - x_2)^2 + \ldots]\ , \tag{16}$$

$$h_2^E = x_1^2\ [A_1 + A_2\ (x_1 - 3x_2) + A_3\ (x_1 - 5x_2)\ (x_1 - x_2) + A_4\ (x_1 - 7x_2)\ (x_1 - x_2)^2 + \ldots]\ . \tag{17}$$

Equations (14) and (15) give the functional dependence of the mean and maximum error of the h^E-measurements from composition x_1, integration error $\Delta A/A$, volume error ΔV and system properties (ρ_i, M_i) and volume V of the components. If no Redlich-Kister parameters of reference data are known parameters calculated from test measurements can be used as first approach.

Model calculations were performed for the systems n-hexane - c-hexane at 25 °C and glycerol - water at 50 °C to evaluate the error limits ΔV and $\Delta A/A$ describing the experimental results. This has to be done in the way that equation (14) describes the mean errors of the experimental results and Δh_{max}^E of equation (15) forms an envelope of all experimental results.

Figures 5 and 6 show the results finally confirming the analysis of errors. It should be noted that figure 6 indicates the high sensitivity of experimental results against metering errors for glycerol - water for high concentrations of glycerol as already to be expected evaluating Figure 5.

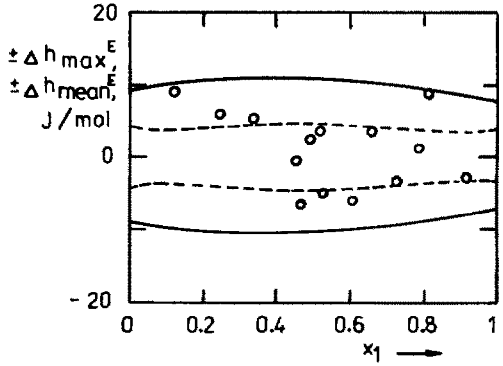

Figure 5: Absolute error of measurements, mean and maximum error for n-hexane (1) - c-hexane (2) at 25 °C for $\Delta V = 0.03$ ml, $\Delta A = 2$ %, $\Delta V_{max} = 0.06$ ml, $\Delta A_{max} = 3$ %

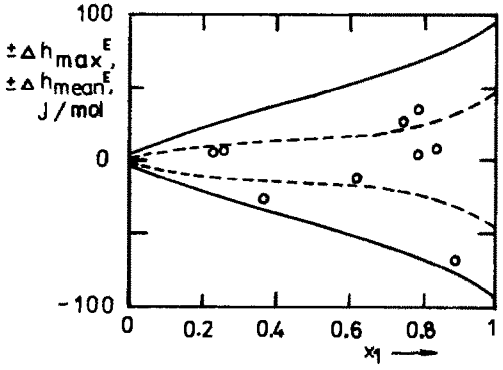

Figure 6: Absolute error of measurements, mean and maximum error for glycerol (1) - water (2) at 50 °C for $\Delta V = 0.03$ ml, $\Delta A = 3$ %, $\Delta V_{max} = 0.06$ ml, $\Delta A_{max} = 6$ %

It should be noted once more that the quantitative sensitivity analysis, as described above, was a decisive information for our analysis of errors. The sources of errors we found at first were metering errors and the inaccuracy of the baseline due to the AD-converter of the data logger. As these errors only (being about 2 % for n-hexane - c-hexane and 4 % for glycerol - water) could not quantitatively explain the experimental errors, a further search for error sources was necessary. This caused us to perform examinations of the baseline over long periods. Thereby we found the influence of random voltage oscillations.

5. RESULTS OF IMPROVED TEST MEASUREMENTS

As result of this analysis of errors following improvements of the equipment were realized:

- Installation of a constant power supply effecting a stable baseline within the limits of the thermovoltage measurement.
- Improvement of the data logger by a better AD-converter (12 bit) and an increase of internal integration time decreasing baseline inaccuracies to values < 0.2 mV according to integration errors < 0.8 % for glycerol - water and < 0.5 % for n-hexane - c-hexane.
- Installation of new pumps with a mean error of 0.003 ml and a maximum error of 0.005 ml.

With this apparatus new test measurements were made for n-hexane - c-hexane at 25 °C. Their results are shown in Figure 7 and listed in Table 7.

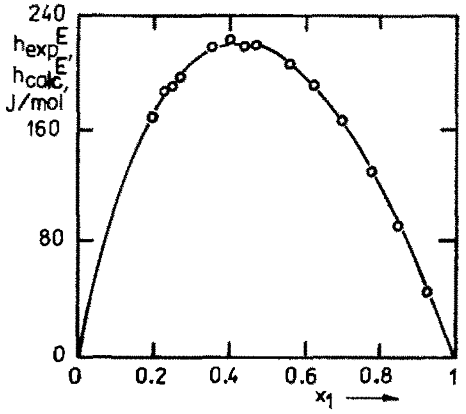

Figure 7: Heat of mixing of n-hexane (1) - c-hexane (2) at 25 °C. o - experimental points, —— correlation of RK expansion

Table 7: Improved measurements for n-hexane (1) - c-hexane (2) at 25 °C

x_1	h_{exp}^E J/mol	h_{calc}^E J/mol	δh_{exp}^E J/mol	h_{ref}^E J/mol	δh_{ref}^E J/mol
0.1929	167.97	167.42	0.55	165.46	2.51
0.2299	186.45	184.18	2.27	182.91	3.55
0.2510	189.53	192.11	-2.58	191.19	-1.66
0.2700	196.27	198.31	-2.04	216.01	2.23
0.4028	222.35	220.37	1.98	220.49	1.86
0.4400	218.87	220.75	-1.88	220.70	-1.83
0.4681	219.34	219.55	-0.21	219.29	0.05
0.5599	206.13	207.19	-1.06	206.09	0.03
0.6253	191.28	190.92	0.35	189.38	1.89
0.6994	166.55	165.42	1.12	163.84	2.70
0.7795	130.15	129.98	0.18	129.05	1.11
0.8503	91.20	92.57	-1.37	92.63	-1.42
0.9301	45.91	44.91	1.00	45.77	0.14

Redlich-Kister-parameters:
A_1 = 866.744 A_2 = 228.157 A_3 = 110.505 A_4 = -107.642
A_5 = 12.958 RMSD = 1.57 J/mol

A Redlich-Kister expansion correlates these new values with a RMSD of 1.57 J/mol corresponding to 0.8 % of the mean of all measured values. The same comparison with data of Marsh [8] produces a RMSD of 1.88 J/mol and 0.9 % of the mean.

6. CONCLUSIONS

Analysis of errors is usually utilized to confirm and judge the reliability of experimental data and equipments. As shown in this contribution, error propagation and sensitivity analysis can be used to calculate the influence of primary errors on the errors of experimental results. This may be a helpful tool for development and improvement as well as tuning of an experimental apparatus. Furthermore it may be helpful to find out limits of equipment concerning substances to be measured and limits of accuracy. Last but not least this procedure could save a lot of time being spent to perform test measurements when done in advance.

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