Measurement and Calculation of Excess Enthalpy with the Isothermal Microcalorimeter

Kwon, Jung Hun

Thermodynamics and Properties Lab.

CONTENTS

I. Introduction

Calorimeter

[1] Three types of calorimeter

: batch calorimeter, displacement calorimeter, flow calorimeter

>> flow calorimeter

(1) To make measurements over a wide range of pressure and temperature conditions

(2) The measurements of the excess enthalpy can be made for gases as well as for liquids

(3) To require large amounts of chemicals

Calorimetric Appartus

[Conditions]

1. Compressed **Helium gas** is used as control gas for back-pressure regulator and backpressure is about 30~40 psi.

2. Pressure is maintained using **back pressure regulator** (the range of 0-3000psi and the accuracy of ±1/4% of 1of span ±7.5psi).

   [to prohibit the evaporation of liquids in the output]

3. **Air bath** (±0.1°C) is set to minimize the effect of the surrounding temperature.

4. **Circulator** is used to maintain the constant temperature of water bath surrounding heat sink.

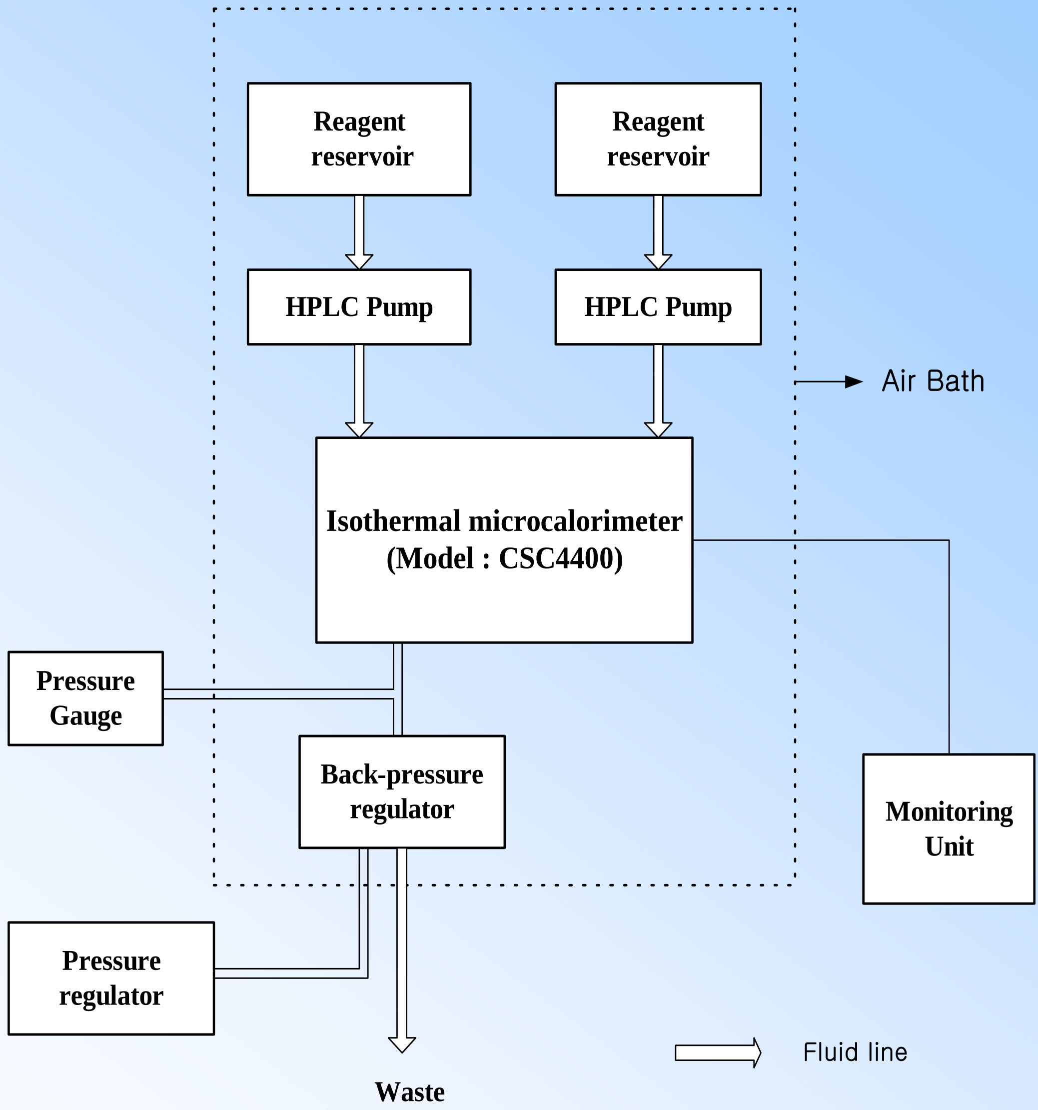
Apparatus of IMC

- Isothermal calorimeter
  - Model CSC 4400 (Calorimetry Sciences Corporation)
- Pump : a set of HPLC pump (Model Acuflow Series II)
- Accuracy of flow rate : ± 2%
- Auxiliary equipments

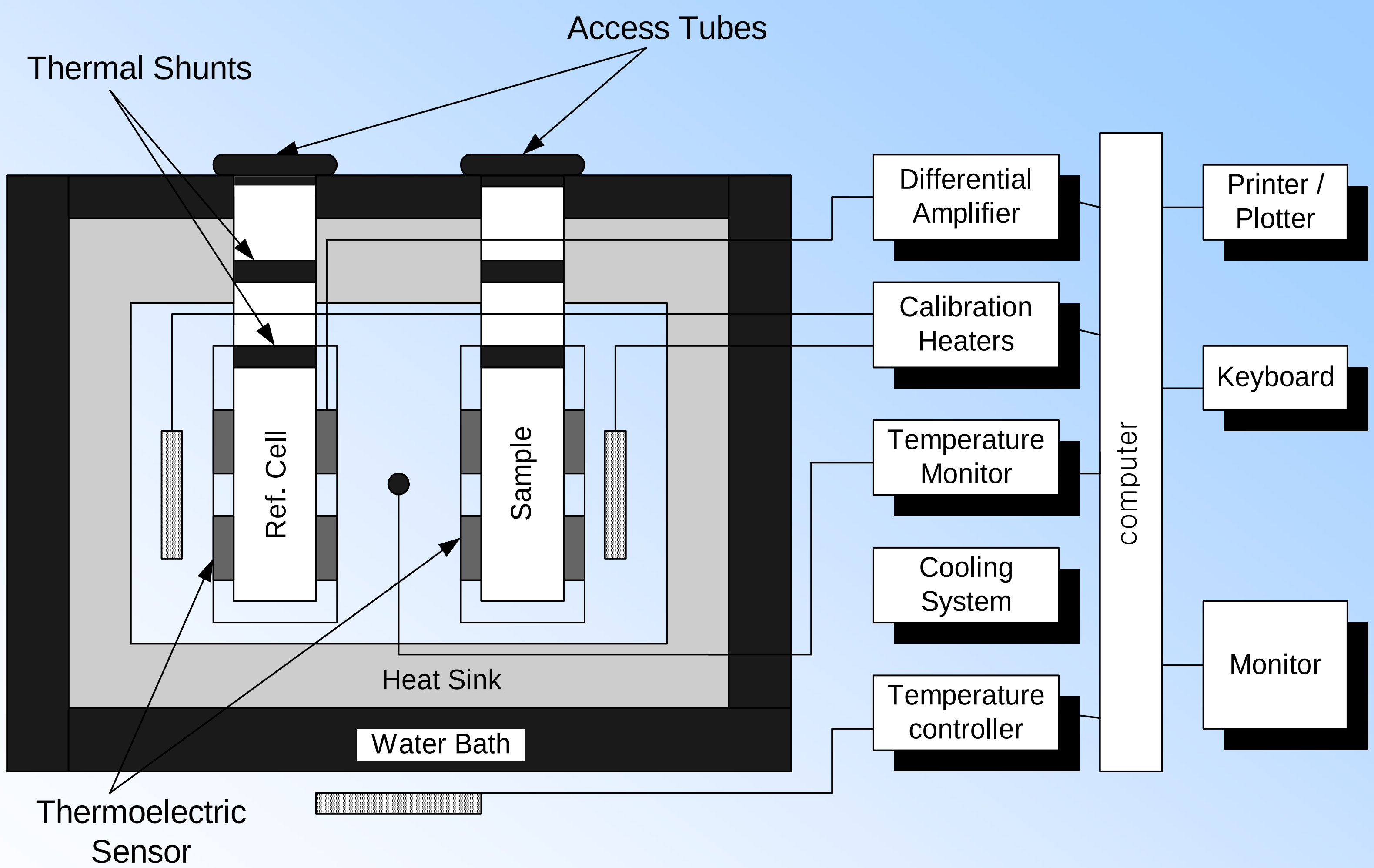
  - Air bath (± 0.1°C) was used to minimize the effects of surrounding

  - Back pressure regulator : the range of 0~3000 psi the accuracy of ± 1/4% of 1 of span ±7.5psi

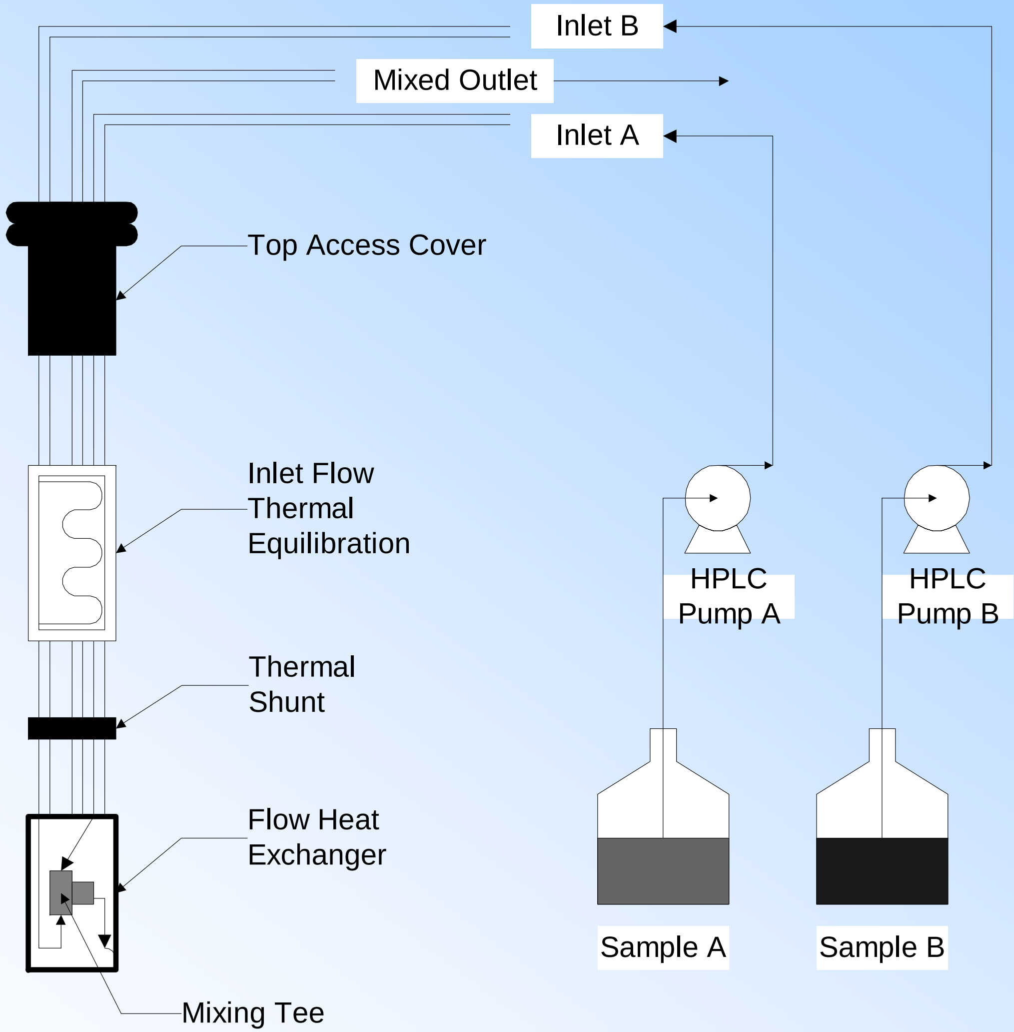
  - Circulator (constant temperature)



Block diagram of experimental Apparatus



Block diagram of IMC



Schematic diagram of flow mixing cell

Thermodynamic Calculations of H^E

- Redlich-Kister
  - the functions of composition and temperature

$$H^E / J \cdot mol^{-1} = (1-x)x\sum_{i=1}^{k} A_i (1-2x)^{i-1}$$

- Wilson, NRTL, UNIQUAC
  - activity coefficient models
- ASOG, UNIFAC, DISQUAC
  - group contribution activity coefficient models
- NLF EOS, Cubic EOS(SRK, PR) etc.

II. Experimental section

Procedure

[1] Determination of the temperature and the pressure

[2] Set to the conditions

$\longrightarrow$ the Isothermal MicroCalorimeter (IMC)

[3] Stabilization of the IMC

[4] Decision of a total flow rate of systems

[5] Determining the base line

[6] Real base lines for the each points

[7] The molar excess enthalpies

[8] Calculation of Excess Enthalpy

II. Experimental section

Analysis & Results

[Pump calibration]

[1] The flow rates of pumps were calibrated by weighing of distilled water that passed through the flow-mixing cell over a period before the measurement of the excess enthalpy.

[2] The accuracies of the measured compositions and excess enthalpies are determined by those of the flow rate and the density.

$$real\ base\ line = (sample\ A's\ base\ line) \times \frac{q_A}{q_T} + (sample\ B's\ base\ line) \times \frac{q_B}{q_T}$$

where, q_i : sample *i*'s flow rate

q_T: total flow rate

II. Experimental section

Results of pump calibration

❍ Pump A

reading flow rate (ml/min)	real flow rate (ml/min)	error (%)	r.m.s
0.1	0.1073	1.87	0.0023
0.15	0.1625	0.06	0.0001
0.2	0.2173	0.24	0.0007
0.25	0.2709	0.18	0.0006
0.3	0.3245	0.28	0.0012
0.35	0.3791	0.06	0.0003
0.4	0.4303	0.74	0.0033
0.45	0.4851	0.61	0.0038
0.5	0.5369	0.87	0.0049
0.55	0.5904	1.11	0.0081
0.6	0.6417	0.72	0.0059
0.65	0.6947	0.82	0.0073

❍ Pump B

reading flow rate (ml/min)	real flow rate (ml/min)	error (%)	r.m.s
0.1	0.112	2.04	0.00258
0.15	0.1648	0.76	0.00166
0.2	0.2218	0.27	0.00067
0.25	0.2765	0.27	0.00082
0.3	0.3329	0.42	0.00174
0.35	0.3853	0.34	0.00165
0.4	0.4376	1.71	0.00959
0.45	0.4818	1.75	0.00876
0.5	0.5378	1.04	0.00696
0.55	0.6011	0.57	0.00433
0.6	0.6391	2.16	0.01584
0.65	0.6908	0.71	0.00523

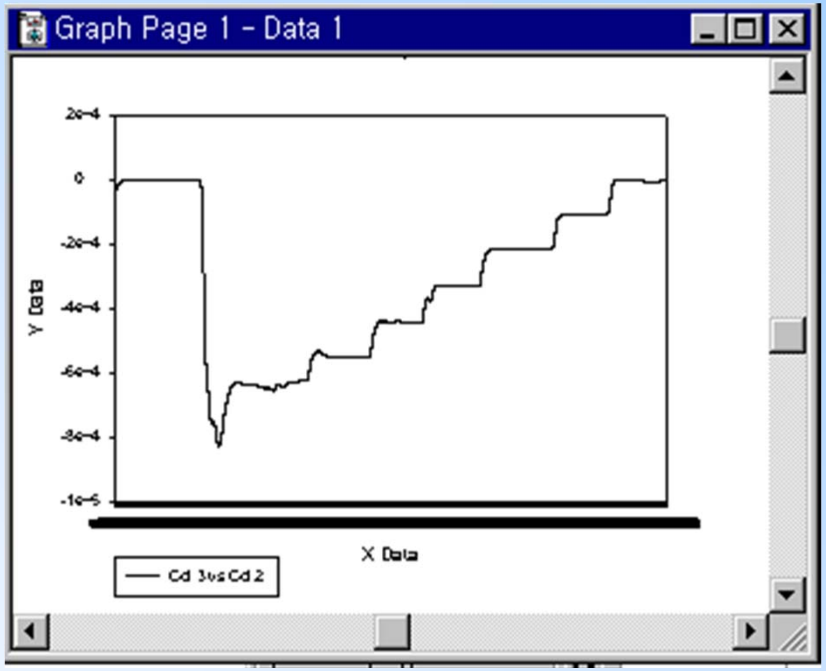
Courses of H^E Calculation

[D a t a]

- The raw data of experiment with IMC

Data 1

	-1-	-2-	-3-
1	29.97	-3863.22	1126.00
2	29.97	-3559.74	1144.02
3	29.97	-3280.90	1162.03
4	29.97	-3024.54	1180.05
5	29.97	-2788.51	1198.01
6	29.97	-2571.02	1216.02
7	29.97	-2370.58	1234.04
8	29.97	-2185.68	1252.00
9	29.97	-2014.81	1270.01
10	29.97	-1857.04	1288.03
11	29.97	-1711.38	1306.05
12	29.97	-1576.48	1324.01
13	29.97	-1451.68	1342.02
14	29.97	-1336.17	1360.04
15	29.97	-1229.12	1378.00
16	29.97	-1129.86	1396.01
17	29.97	-1037.88	1414.03
18	29.97	-952.60	1432.04
19	29.97	-873.34	1450.01
20	29.97	-799.80	1468.02
21	29.97	-731.44	1486.04
22	29.97	-667.85	1504.00
23	29.97	-608.78	1522.01
24	29.97	-553.80	1540.03
25	29.97	-502.64	1558.04
26	29.97	-455.05	1576.00
27	29.97	-410.68	1594.02
		Plot 1 Y Data	Plot 1 X Data



X data : time

Y data : enthalpy

II. Experimental section

Calculation Method (Example)

Reagent	Density	M . W
Water	0.997	18.02
1 -butanol	0.80206	74.13

Pump B Water	Pump A 1 -butanol	real flow rat of pump B	real flow rat of pump A	mole flow rat of pump B	mole flow rat of pump A	total flow rate	calory (micro Watt)
0	0.65	0	0.6976	0	0.007547782	0.007547782	284.0646
0.1	0.55	0.1047	0.603	0.00579278	0.006524244	0.012317024	-65866.20
0.15	0.5	0.1682	0.5471	0.009306071	0.005919426	0.015225497	-55080.5
0.2	0.45	0.2178	0.4918	0.012050311	0.0053211	0.01737141	-43957.2
0.25	0.4	0.2741	0.4377	0.015165244	0.004735757	0.019901001	-32641.8
0.3	0.35	0.3263	0.3848	0.018053335	0.004163398	0.022216733	-21520.9
0.35	0.3	0.3795	0.3374	0.020996754	0.003650547	0.024647301	-10636.2
0.4	0.25	0.4324	0.274	0.023923574	0.002964582	0.026888155	-379.307
0.45	0.2	0.4862	0.2196	0.026900189	0.002375993	0.029276182	6822.136
0.5	0.15	0.5414	0.1635	0.029954262	0.001769011	0.031723273	16399.98
0.55	0.1	0.5942	0.1092	0.032875549	0.001181505	0.034057054	25583.19
0.65	0	0.6943	0	0.038413824	0	0.038413824	269.8025

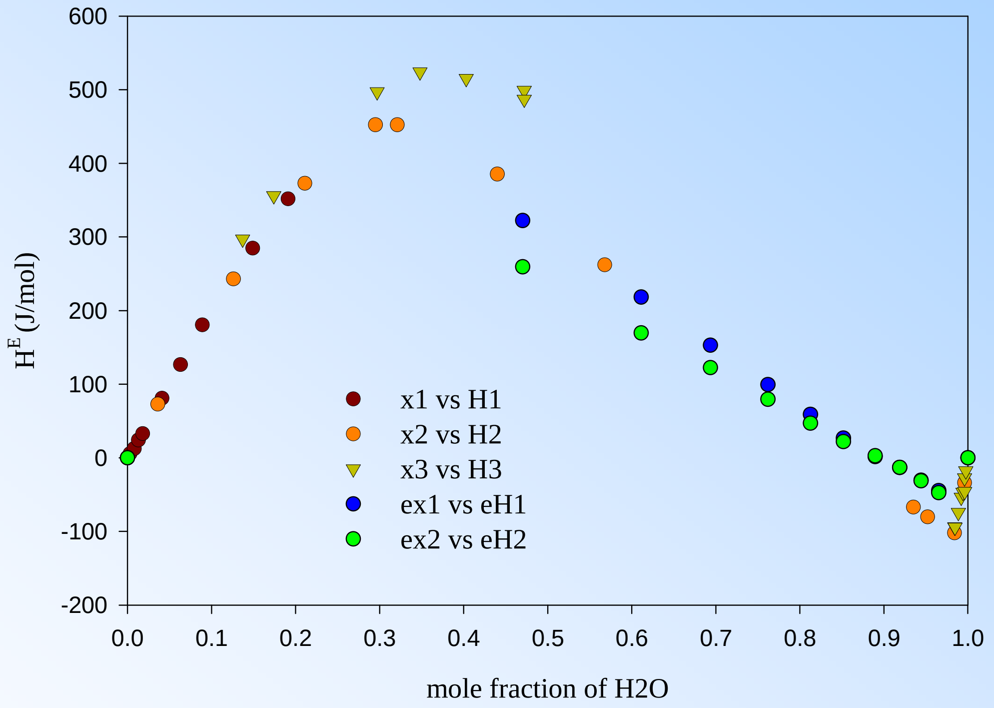
composition Pump B = x	composition Pump A = (1 -x)	Base line	final calory			Calory (J/mol)	
0.0000	1.0000	284.0646	0			0	
0.4703	0.5297	281.9546072	66148.15461			322.2279439	
0.6112	0.3888	280.7109229	55361.21092			218.1651421	
0.6937	0.3063	279.687084	44236.88708			152.7920405	
0.7620	0.2380	278.5725494	32920.37255			99.25241156	
0.8126	0.1874	277.5201995	21798.4202			58.8702761	
0.8519	0.1481	276.5147786	10912.71478			26.56529812	
0.8897	0.1103	275.334515	654.641515			1.460810167	
0.9188	0.0812	274.239957	-6547.896043			-13.41956968	
0.944236166	0.055763834	273.1105626	-16126.86944			-30.50164963	
0.965308074	0.034691926	272.0166332	-25311.17337			-44.59194835	
1	0	269.8025	0			0	

II. Experimental section

R e s u l t

	-1- x1	-2- H1	-3- x2	-4- H2	-5- x3	-6- H3	-7- ex1	-8- eH1	-9- ex2	-10- eH2
1	3.00e-3	5.53	0.04	72.85	0.14	297.00	0.00	0.00	0.00	0.00
2	0.01	12.35	0.13	242.83	0.17	356.00	0.47	322.23	0.47	259.31
3	0.01	24.07	0.21	372.63	0.30	497.00	0.61	218.17	0.61	169.53
4	0.02	32.74	0.30	452.17	0.35	524.00	0.69	152.79	0.69	122.38
5	0.04	80.81	0.32	452.17	0.40	515.00	0.76	99.25	0.76	79.44
6	0.06	126.44	0.44	385.19	0.47	499.00	0.81	58.87	0.81	47.05
7	0.09	180.45	0.57	262.09	0.47	487.00	0.85	26.57	0.85	21.79
8	0.15	284.70	0.94	-66.99	0.98	-93.90	0.89	1.46	0.89	2.72
9	0.19	351.69	0.95	-80.39	0.98	-94.30	0.92	-13.42	0.92	-13.07
10			0.98	-102.16	0.99	-74.30	0.94	-30.50	0.94	-31.38
11			1.00	-33.91	0.99	-53.50	0.97	-44.59	0.97	-47.42
12					0.99	-47.00	1.00	0.00	1.00	0.00
13					1.00	-27.30				
14					1.00	-45.90				
15					1.00	-17.60				

II. Experimental section



Excess Enthalpy for H_2O + 1-Butanol

III. Conclusion

[1] Accuracy of isothermal calorimeter was confirmed, the excess enthalpies were measured for water + 1-butanol at 298.15K

[2] The relative error for each system was within 10%.
……. [water +1-butanol at 298.15K]

[3] Measurements and calculations of excess enthalpy for binary system can be accomplished with the Isothermal Microcalorimeter.