資 料

Netsu Sokutei 10(4) 152–157 (1983)

Calorimetry Research Activities in China*

Hu Ri-heng（胡日恒）

Institute of Chemistry, Academia Sinica,
Beijing, China

This was an invited lecture delivered at the 18th Annual Meeting of the Japan Society of Calorimetry and Thermal Analysis, in which a brief account of the historical development of calorimetry researches in China was given and then followed a description of some typical research activities in several Chinese calorimetry laboratories. The activities of the Commission on Thermodynamics, Thermochemistry and Thermal Analysis, the Chinese Chemical Society (CCTTT) and some visits of the scientists in these fields from the other countries were described.

Ladies and Gentlemen:

It is a great honor and pleasure for me to have the chance to deliver a speech to you on "The Calorimetry Research Activities in China". I hope that it will be useful for promoting mutual understanding and possible cooperation between the scientists in these particular fields of our two neighboring countries.

Before the establishment of the People's Republic of China in 1949, there was not much research work in calorimetry and thermal analysis in China. By the time from late fifties to early sixties, the Chinese calorimetry scientists gradually realized that calorimetry is basically an experimental science and it is of first importance for us to build our own instruments and to obtain our own experimental data to solve our own problems. Professor Huang Tzu-ching（黃子卿）of Peking University（北京大學）, Beijing, and Professor Feng Shi-yan（馮師顏）of Northwest University（西北大學）, Xian（西安）, Shanxi Province（陝西省）, were among the most consistent advocates of such a necessity of instrument development. Prof. Huang was one of my former professors when I was a college student. He maintained a large laboratory on "Solution Research" when Dr. Zhang You-min（張行民）who had stayed for several years in Soviet Union came back. He helped set up a Solution Calorimetry Section in Prof. Huang's Solution Research Laboratory. He is now studying the thermochemistry of solvation of ions in polar solvents. Prof. Feng was a good friend of mine. He had spent several years in Moscow University in Prof. S. M. Skuratov's Thermochemistry Laboratory and was thus well versed in Experimental Thermochemistry. A kind of division of labor was informally agreed upon between us that he should spend more effort on low temperature heat capacity calorimetry while I on bomb combustion calorimetry. He had the support of the Provincial Bureau of Education and his university and established a large Thermochemistry Laboratory of about twenty persons and helped set up a subdepartmental division in the Chemistry Department of the Northwest University to train students in Thermochemistry. He died during the "Chinese Cultural Revolution", but this laboratory somehow survived it and now Dr. Shen Jie-ru（申潔如）, a lady scientist, is the director of the laboratory. The Institute of Chemical Physics, Academia Sinica, in Dai-lian（大連）, Liaoning Province（遼寧省）, on the tip of Liao-dong Peninsula（遼東半島）, started their thermochemistry research a little later under the leadership of Prof. He Xue-lun（何學倫）. He lost his sight, becoming a blind man in the late sixties, and was forced to retire. A team of his

---

* 本稿の内容は1982年10月に東北大学選鉱研で開催された第18回熱測定討論会における中国化学院 化学研究所　胡日恒教授の特別講演である。執筆依頼の労をとられた大阪大学理学部　菅　宏教授に感謝いたします（編集委員会）。

young associates took over, turned their research direction from bomb combustion calorimetry to low temperature heat capacity works and built a nice low temperature heat capacity calorimeter of which I will talk presently. It is an adiabatic calorimeter for heat capacity measurements of solids and liquids in the temperature range of 80–370 K. The main body of the calorimeter consists of a sample container, an outer and an inner adiabatic shield, an upper ring for preheating lead wires and a vacuum can. The sample container is made of silver of 99.95% purity, 0.3mm thick, gold-plated and polished, and is provided with a central well for admitting a thermometer-heater assembly. The total weight of the container is about 50 g and its effective volume is *ca.* 40 cm^3. The temperature of the container is measured with a platinum resistance thermometer and a Smith Bridge of English make. The thermometer which is Pt-encapsulated, 25 Ω, 5 mm in diameter and 50 mm long, was made by Yunnan Instrument Manufacturing Company, Yunnan Province (雲南省), China on special order and calibrated at the Chinese Academy of Metrology (計量研究所), Beijing, China in accordance with the IPTS-68. The temperature difference between the container and the inner shield and those between shields are detected by 3 eight junction copper-constantan thermocouples and controlled independently by 3 DWT-702 type controllers of Chinese make. Experiments demonstrated that, during the heat capacity measurements, the temperature difference between the inner shield and the container could be kept within 0.002 K. For electric energy measurements, a UJ-25 potentiometer of Chinese make was used. The precision of the energy input was better than 0.01%.

The reliability of the apparatus was examined through the heat capacity measurements of α-Al_2O_3(c) and the n-heptane(l) which are recommended as the heat capacity standards. The purities of the α-Al_2O_3 and the n-heptane samples used in these measurements are 99.993% and 99.99%, respectively. The results of these measurements are presented in Table 1 and Table 2 and in which comparisons with US NBS's values are being made, the max. difference being about 0.2%. This is probably the limit of reliability of the instrument developed in the Institute of Chemical Physics, Academia Sinica at the present stage.

I believe that the temperature range of the calorimeter could be extended to liquid hydrogen temperatures without much modification but no liquid hydrogen was available to them at the time when these measurements were made. If, however, they want to go down to the liquid helium temperatures, a modification of the coolant bath to save liquid helium must be made, because helium is rather expensive in China. In fact, Mr. Tan Zhicheng (譚志誠) of the group has been cooperating

Table 1. Molar heat capacities of α-Al_2O_3(c)

T	C_p (J K^{-1} mol^{-1})		Diff.	T	C_p (J K^{-1} mol^{-1})		Diff
K	This work	US NBS	(%)	K	This work	US NBS	(%)
85	8.255	8.246	0.10	230	61.09	61.10	−0.02
90	9.714	9.692	0.22	240	64.16	64.13	0.05
100	12.80	12.84	−0.31	250	66.93	67.01	−0.12
110	16.28	16.32	−0.24	260	69.62	69.76	−0.20
120	20.04	20.06	−0.10	273.15	72.99	73.16	−0.23
130	23.97	23.96	0.04	280	74.78	74.84	−0.08
140	27.96	27.96	0	290	77.17	77.19	−0.03
150	31.98	31.98	0	300	79.43	79.41	0.03
160	36.01	35.99	0.06	310	81.61	81.51	0.12
170	39.95	39.94	0.03	320	83.61	83.50	0.13
180	43.81	43.79	0.05	330	85.49	85.39	0.12
190	47.65	47.53	0.25	340	87.24	87.18	0.07
200	51.02	51.14	−0.23	350	88.90	88.88	0.01
210	54.73	54.60	0.24	360	90.40	90.52	−0.13
220	58.06	57.92	0.24	370	91.89	92.06	−0.18

Table 2. Molar heat capacities of n-heptane (M.W. 100.20)

T / K	C_p (J K^{-1} mol^{-1}) This work	C_p (J K^{-1} mol^{-1}) US NBS	Diff. (%)	T / K	C_p (J K^{-1} mol^{-1}) This work	C_p (J K^{-1} mol^{-1}) US NBS	Diff. (%)
200	201.65	201.31	0.17	290	221.48	221.75	−0.12
210	201.98	201.68	0.15	300	225.26	225.44	−0.07
220	202.53	202.74	−0.10	310	229.03	229.27	−0.10
230	204.71	204.36	0.17	320	233.14	233.25	−0.04
240	206.47	206.47	0	330	237.20	237.38	−0.07
250	208.86	208.93	−0.03	340	241.31	241.67	−0.14
260	211.55	211.73	−0.08	350	246.09	246.09	0
270	214.98	214.81	0.08	360	250.91	250.63	0.11
280	218.42	218.23	0.09	370	255.31	255.30	0.02

with the Chinese Academy of Metrology to construct a calorimeter with the temperature range down to 5 K to provide some standard samples to the calorimetry laboratories in China. They are planning to use the calorimeter to study surface adsorption phenomena of solids, which is in line with one of the major research activities, the study of catalysis, of their institute. In Northwest University, Xian, Shanxi Province, China, a similar set-up with similar level of accomplishment has also been built. They installed a helium liquefier in 1980 and should have no problem to go down to the liquid helium temperatures.

The second piece of equipment that I am going to report to you is a static-bomb combustion calorimeter of Dickinson type constructed in our laboratory, the Thermochemistry Laboratory of the Institute of Chemistry, Academia Sinica, Beijing, China. It is a water-cap type of arrangement. The water bath was controlled at 22.5 ± 0.001°C and the whole apparatus was housed in a cabinet, its temperature being regulated at 22.5 ± 0.2°C. A platinum resistance thermometer and a Smith Bridge were used for temperature measurement, its sensitivity being better than 0.0002°C. The energy equivalent of the calorimeter was obtained electrically and the results of the electrical calibration are shown in Table 3. The reason for undertaking the rather exacting and tedious work of electrical calibration was a historical one, because we were then unable to obtain benzoic acid with a certified value for its combustion heat. To further test the reliability of the instrument, we prepared a batch of pure benzoic acid with purity of 99.999% established by the melting curve of the pure sample and those mixed with various known amounts of impurity (anthracene). Since heat of combustion of benzoic acid has been determined by many laboratories and well-documented and its value for samples of purity of 99.99% or higher would not differ significantly from each other, we decided to measure the heat of combustion of the benzoic acid sample prepared by us. Table 4 gives the results of the combustion experiments. The error is expressed in an "uncertainty internal", i.e.,

Table 3. Electrical determinations of the energy equivalent of the calorimeter

No.	$\Delta\theta_{\text{corr.}}$ / Ω	voltage / V	current / A	Δt / s	W / J	$K\cdot10^3$ / °C/Min°C	$u\cdot10^4$ / °C/Min	ε_{si} / J/Ω
1	0.139831	72.4005	1.48849	320.356	34523.9	1.854	0.83	24689_7
2	0.149811	72.3370	1.48741	343.819	36993.1	1.842	1.34	24693_2
3	0.138225	72.4587	1.49028	316.038	34127.0	1.854	1.00	24689_4
4	0.142825	72.4554	1.49090	326.502	35270.0	1.831	1.48	24694_5
5	0.142434	72.5069	1.49205	325.050	35165.2	1.833	0.97	24688_8
6	0.144186	72.4397	1.49086	329.532	35588.6	1.835	1.61	24682_4
7	0.139996	72.5039	1.49240	319.343	34554.5	1.833	1.17	24682_5
8	0.142558	72.3714	1.49006	326.316	35189.2	1.843	1.39	24684_1

$\varepsilon_{\text{si}} = (24688_1 \pm 16.3)$ J/Ω or ±0.007%

Table 4. Results of benzoic acid combustion experiments
$\varepsilon_i = 246907\ \mathrm{J/\Omega}$ $f = 1.00019_1$

No.	m_s(Vac.) g	$\Delta\theta_{corr.}$ Ω	$K\cdot10^3$ °C/Min°C	$u\cdot10^4$ °C/Min	Q_B J	q_i J	q_n J	$-\Delta E_B$(22.3°C) J/g	$-\Delta E_B^c$ J/g
1	1.31156	0.140573	1.849	1.61	34708.5	31.5	8.8	26432.8	26427.7
2	1.31341	0.140769	1.833	1.89	34756.9	25.7	8.4	26437.1	26432.0
3	1.29315	0.138585	1.831	1.52	34217.6	16.7	8.6	26441.1	26436.0
4	1.31370	0.140788	1.828	1.55	34761.5	16.8	8.3	26441.7	26436.6
5	1.30734	0.140116	1.838	1.76	34595.6	16.0	8.2	26444.1	26439.0
6	1.30336	0.139611	1.837	1.27	34472.4	13.8	8.0	26432.2	26427.1
7	1.30180	0.139468	1.841	1.56	34435.6	16.7	8.0	26433.3	26428.2
8	1.31612	0.141032	1.841	1.46	34821.8	16.3	3.4	26443.0	26437.9

$-\Delta E_B^c = (26433.1 \pm 1.7)\ \mathrm{J/g}$ or ± 0.006%.

twice the total standard deviation of the mean. It can be seen in Table 3 and Table 4 that the Newton's cooling constant K's in all electrical calibration and benzoic acid combustion runs do not deviate from each other more than 0.3%, but the heat of stirring u's differ from each other considerably. This raises the question: How reliable is the u value in each experiment, which is used implicitly for calculating the corrected temperature rise? A special experiment was thus devised in which different stirring speeds were used, but otherwise the experimental conditions remained the same. In Figure 1, a plot of u vs n^3 (rpm^3) gives a straight line passing approximately through the origin, indicating that the individual u can be determined to 5–10%, and the evaporation from the calorimeter liquid to its surrounding or *vice versa*, has been effectively eliminated. In Table 5, there give the values of heat of combustion of benzoic acid from our laboratory and those determined by other laboratories in different years. In this work we were cooperating with the Chinese Academy of Metrology. They not only calibrated our electrical instruments, but also lent us a quartz time piece for our input energy measurements. Later on, they built a similar calorimeter with a slightly better precision, presumbly they had better measuring equipments. The work was completed in about 1965, just before the start of the "Chinese Cultural Revolution". Now, we have also constructed a rotation bomb combustion calorimeter with similar precision and accuracy, the platinum resistance thermometer being replaced by a quartz oscillating thermometer of U.S. H.P. Company and its energy equivalent calibrated by the U.S. NBS standard benzoic acid. We are currently using it to study some chlorine containing organic compounds.

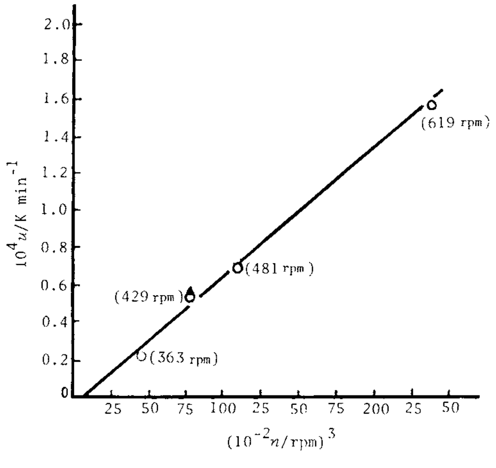

Figure 1. The Relationship between the stirring heat and the stirring speed.
o denotes a series of experiments. ▲ denotes an additional experiment. rpm is revolutions/min.

The third equipment is a Tian-Calvet twin type conduction calorimeter constructed by Dr. Deng-Yu (鄧郁) and his group at Si-chuan University (四川大學), Chemistry Department, Cheng-du (成都), Si-chuan Province (四川省). Each element of the twin has 72 Chromel-constantan thermocouples in series affixed on 12 aluminium flat rings which are placed between the calorimeter vessel and its inner jacket. The vessels are quite large approximately 60 cm^3 each, thus having a large effective heat capacity, μ, and this together with the small number of thermocouples employed

Table 5. Comparison of the heat of combustion of benzoic acid determined by different laboratories

Investigators	year	country	$-\Delta E_B^\circ$ (J/g)
Jessup & Green	1934	U.S.A.	26432.0
Jessup	1942	U.S.A.	26433.8
Prosen & Rossini	1944	U.S.A.	26434.7
Coops, Van Nes & Schaafsma	1951	Netherlands	26437
Challoner, Gundry & Meetham	1955	U.K.	26436
Coops & Adriaanse	1956	Netherlands	26435
The authors of this work	1966	China	26433
Churney & Armstrong	1968	U.S.A.	26434.4
Gundry, Harrop, Head & Lewis	1969	U.K.	26434.4
Mosselman & Dekker	1969	Netherlands	26432.7
Aleksandrov *et al.*	1974	Soviet Union	26436.6

in the setup would make the response time of the instrument unduly long but for the intervening of the Al-rings, which greatly increase the thermal conductivity between the calorimeter vessel and its inner jacket. Of course, there is a price of sensitivity lowering to pay, but this apparatus was meant to be of semimicro-range and the ease for assembling the thermocouples makes it profitable to adopt such an arrangement.

Performance: The heat transfer coefficient, k, which converts the area under a curve traced on the recorder to the heat quantity generated in the experimental cell was determined in a series of measurements to be $(1.887 \pm 0.003) \cdot 10^{-3}$ cal/mm^2 and the response time to be (6.30 ± 0.01) minutes. Thus, for a heat quantity of about 10 cal, an area of about 5000 mm^2 would be traced on the recorder; for a heat power of 0.01 cal/s, a peak height of about 60 mm would appear. In the energy range mentioned, a precision of 0.5% might be expected from their instrument. Dr. Deng and his group have used it to determine the amount of CO_2 produced in some reactions by measuring the heat of absorption of CO_2 in KOH solution and provide a convenient method for evaluating the effectiveness of catalysts to remove CO_2 in the ammonia synthesis plant. It has also been used to investigate the setting characteristics of cements of different brands produced in China.

I select these three equipments to report to you, because I think though there are many variations, these are still the three major basic types of calorimetry art, and thus I hope it would be possible for me to convey to you to what extent that we have mastered the arts of calorimetry, that might be useful for initiating some kinds of co-operation between the scientists of our two countries.

For Chinese thermal analysts, I shall mention very briefly. Though thermal analysis technique has been employed, for examples, in the study of salt lake phase diagrams and in the ceramic industry for a long time, the quite recent boom in its activities was largely due to the much wider application to the material property studies. Many of them were associated with different material science laboratories and considered themselves as the research workers of the particular material sciences in which they were engaged rather than as thermal analysts, making their total number difficult to know. This situation has been somewhat remedied since 1979 when an effort to get together was made. All I can say at the moment is that they outnumber the chemical thermodynamics and calorimetry workers together perhaps three to one and that they seldom make their own equipments, but rather depend on the instrument makers (both domestic and foreign) to supply them with instruments. Quite a few foreign friends of mine wrote to me to require informations about the thermal analysis activities in China, but since I am a calorimetry worker myself, I think it would be more suitable for me to find a collaborator who is a thermal analyst and willing to spend some effort to undertake a survey of the situation and then to write a separate communication for foreign readers.

Now I will talk about the organization and community activities of Chinese workers in calorimetry and thermal analysis. In 1979, the Chinese Chemical Society set up the Commission on Thermodynamics, Thermochemistry and Thermal Analysis, abridged as CCTTT. Prof. Huang Tzu-ching of Peking University, Beijing, was elected as the Chairman of CCTTT. Unfortunately, he died in July, 1982, at the age of 82. In 1980, the first Symposium of CCTTT was held in Xian, Shanxi Province, with about 130 persons participating in the meeting and 108 papers presented in three sections. The next meeting has been scheduled in 1984, subjected, of course, to the conformation of the Chinese Chemical Society. We hope that there will be some Japanese guests coming to our meeting at that time. During "the Chinese Cultural Revolution", we were living in seclusion, but beginning in 1977, we have had some limited contacts with the scientists from foreign countries. In 1979, we visited Thermochemistry Laboratory, Lund University, Sweden, Prof. Stig Sunner was still living. In 1980, Prof. Edgar Westrum, Jr., of Michigan University, Ann Arbor, and his wife were visiting us, staying in Beijing for a week, and then went with us to Xian where he gave a lecture at the general session of the Symposium and a series of lectures on low temperature heat capacity measurement and interpretation at the Northwest University. In 1981, Prof. and Mrs. Wadsö of Lund University were with us. Unluckily, he caught cold — he blamed the Asian virus that he was not immune to — and stayed in bed for most of time. In the same year, Prof. Finch of London University came to China, lecturing at the beautiful campus of Wuhan University（武漢大學）on the southern bank of Yantze River. He apparently didn't come to Beijing. I didn't meet him. This year, he sent one of his associate, Dr. Smith, a young lady, to Wuhan University to do some research on bond energy of organic boron compounds, using their rotation bomb combustion calorimeter, and, of course, in May, Prof. Seki and Prof. Suga visited us, but they could only stay for nine days. It was really too short to visit a country of China's size. Now I am here with you. "Seeing is believing" as Prof. Suga put it. I am sure I will be more familiar with the works that you have been doing. Thank you.

References

(1) Tan Zhi-cheng, Zhou Li-xing, Yin An-xue, Chen Shu-xia, Sun Yi, and Wang Xian-liang, *Acta Chimica Sinica* **38**, 511 (1980).

(2) G.T. Furukawa, T.B. Douglas, R.E. McCoskey, and D.C. Ginnings, *J. Res. Nat. Bur. Stand.* **57**, 67 (1956).

(3) T.B. Douglas, G.T. Furukawa, R.E. McCoskey, and A.F. Ball, *J. Res. Nat. Bur. Stand.* **53**, 139 (1954).

(4) Hu Ri-heng, An Shui-wu, and Tan Fu, *Acta Chimica Sinica, Additional Volume,* 18 (1981).

(5) Tian An-ming, Qin Zi-ming, Zeng Xian-cheng, Zhan Shu-guang, and Deng Yu, *Chemical Journal of Chinese Universities,* **2**, 244 (1981).