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CONSTRUCTION AND TESTING OF A GAS–SOLID REACTION CALORIMETRY SYSTEM USING A TIAN–CALVET MICROCALORIMETER *

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ABSTRACT

A gas–solid calorimetry system has been constructed, in which a Tian–Calvet microcalorimeter (low temperature model) and a gas-manipulation facility are incorporated. This system was tested for the reaction $NiCl_2(cr) + 6NH_3(g) = [Ni(NH_3)_6]Cl_2(cr)$ at 351 and 362 K. The derived enthalpy changes were reduced to the value at 298.15 K, which agreed with the value based on the literature data of standard enthalpies of formation of the species that participate in the above reaction.

INTRODUCTION

Thermodynamic studies of gas–solid heterogeneous systems have been carried out, in most cases, by means of equilibrium pressure measurement at various temperatures. By analyzing p–T data, partial molar enthalpies $\Delta_r\overline{H}^\ominus$, entropies $\Delta_r\overline{S}^\ominus$ and Gibbs energies $\Delta_r\overline{G}^\ominus$ are obtained. However, for the two former quantities, derived values are the mean values for the measured temperature range. Furthermore, when the composition of a non-stoichiometric solid phase in equilibrium with a gas phase depends on temperature, the above-mentioned method may not be applied in principle. Simultaneous and independent determinations of enthalpy and Gibbs energy changes by calorimetry and equilibrium pressure measurement, respectively, are free from these problems and are thus more favorable [1]. Since a prolonged period is required for a gas–solid reaction, owing to the slow diffusion of the gas through the solid phase, Tian–Calvet-type microcalorim-

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eters with high sensitivity and long-term stability of the base line have been used for metal–hydrogen [1–6] and metal–oxygen [7–20] systems.

In this paper, a gas–solid reaction calorimetric system, incorporating a Tian–Calvet microcalorimeter, with a gas manipulation facility for the determination of equilibrium pressure and of the amount of gas reacted, is described. This system was tested by calorimetric determination of the enthalpy of the reaction

$$\mathrm{NiCl_2(cr) + 6NH_3(g) = [Ni(NH_3)_6]Cl_2(cr)} \qquad (1)$$

This reaction is known to proceed rapidly and to be completed in 1 h for partially ammoniated nickel dichloride [21]. Standard enthalpies of formation at 298.15 K of the relevant species are available in the literature [22,23].

EXPERIMENTAL

The gas–solid reaction calorimetry system

A schematic diagram of the system is shown in Fig. 1. This system consists of calorimetric and gas-manipulation sections.

Calorimetric section

In this section, a Tian–Calvet microcalorimeter [24] (Setaram, low temperature model, from 77 to 473 K) with a sensitivity of about 60 μV mW^{-1} and two identical reaction vessels are included. In the experiments, the temperature of the isothermal block of the calorimeter was controlled by use of a proportional-integral temperature controller (Setaram RT-3000), under cooling with cold nitrogen gas flow (flow-mode) when required.

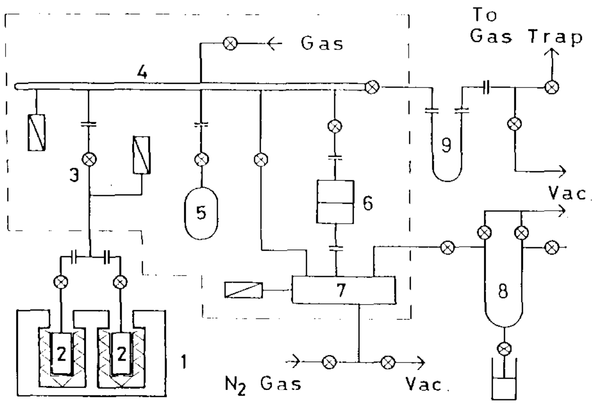

Fig. 1. Schematic diagram of the gas–solid reaction calorimetry system: ⬚, air thermostat; ⊗, greaseless stop-cock; ⊣ ⊢, joint; ▨, pressure gauge (strain gauge type); 1, calorimeter 2, reaction vessel; 3, needle cock; 4, gas-manipulation line; 5, reference volume vessel; 6, differential pressure gauge (MKS) 7, ballast tank; 8, Hg manometer; 9, cold trap.

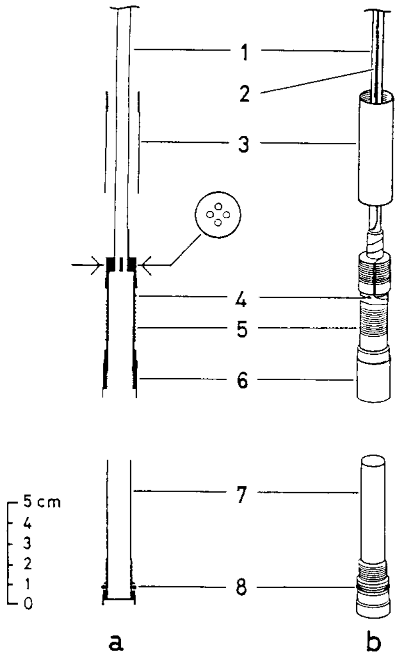

Fig. 2. Side and cross-sectional views of the reaction vessel: 1, stainless-steel tube; 2, lead wire; 3, cover; 4, thermocouple; 5, heater wire; 6, reaction vessel; 7, sample container; 8, O-ring.

Cross-sectional and side views of the reaction vessel are shown in Fig. 2. The vessel is connected to the gas-manipulation section through a greaseless stop-cock on its top and a stainless steel tube with internal diameter of 2 mm and length of 100 cm. The reaction vessel proper (6) and the sample container (7) are made of stainless steel. At the neck of the reaction vessel proper, there are four small holes, through which gas enters or leaves the vessel. The internal volume below the neck is about 6.7 cm^3. The vessel is equipped with a calibration heater (Nichrome V, about 500 Ω) wound around the external surface of the reaction vessel proper, and a thermocouple junction (chromel to constantan) for temperature measurement.

Output voltage from the calorimeter was measured with a 6.5 digits digital multimeter (Keithley 181) and, at the same time, recorded on a strip-chart recorder. The digital data acquisition and processing were carried out with a personal computer (NEC PC-8001).

Gas-manipulation section

This section consists of a Pyrex glass tube ("line") (4) about 100 cm^3 in volume, a reference volume vessel (5) 98.630 ± 0.019 cm^3 in volume, and pressure measurement facilities (6,7,8). The section can be evacuated to 2×10^{-4} Pa. The whole section, except the mercury manometer (8), was placed in an air thermostat kept within 301 ± 0.05 K. Temperatures were measured at both sides of the tube and the average of the two was adopted as the temperature of the gas in this section.

The pressure of gas in this section was determined by measuring the pressure difference between the line and the ballast tank (7) with a capacitance pressure gauge (MKS type 222A, ±1.333 kPa in full scale, ±1.5% of reading in accuracy) and the pressure in the ballast tank with a mercury manometer (8). The capacitance gauge was placed in the air-thermostat and calibrated against the mercury manometer. By this procedure, the inaccuracy of the gauge was decreased to 0.7% of the reading. By use of the mercury manometer, pressures up to 66.6 kPa (500 torr) were measured with a resolution of 1.3 Pa (0.01 torr) and those between 35 kPa (260 torr) and 160 kPa (1200 torr) were measured with a resolution of 13 Pa, which is equal to the resolution of a mercury barometer. The section is equipped with three auxiliary strain-gauge-type pressure gauges in order to monitor the pressure in each part, as shown in Fig. 1.

Test experiments

Materials

Nickel dichloride hexahydrate (Wako, G.R.) was recrystallized from aqueous solutions three times, and dehydrated at 473 K under a stream of nitrogen. Anhydrous nickel dichloride thus obtained was purified by sublimation (twice) at 873 K in vacuo [21]. Analysis: found: Ni, 45.15%; Co, 0.0072%; Fe, 0.0027%, calculated for $NiCl_2$: Ni, 45.29%. The value of the density used for buoyancy correction was 3.521 g cm^{-3} [25].

Commercial ammonia (Seitetsu Kagaku, 99.99% in purity) was used after drying over soda lime.

Gas–solid reaction calorimetry

The amount of gas reacted $n(NH_3)$ was obtained as the decrease in the amount of gas in the gas-manipulation line Δn(line) minus the increase in the reaction vessels and inlet tubes Δn(vessels)

$$n(NH_3) = \Delta n(\text{line}) - \Delta n(\text{vessels}) \qquad (2)$$

For the calculation of the amount of gas reacted the following equation of state was employed

$$pV = nRTZ(p,T) \qquad (3)$$

where V is the volume of gas at temperature T and pressure p and n is the amount of gas. $Z(p,T)$ is the compressibility factor defined as

$$Z(p,T) = 1 + \frac{9(p/p_c)}{128(T/T_c)}\left[1 + \left(\frac{T}{T_c}\right)^2\right] \qquad (4)$$

where T_c and p_c are the critical temperature and pressure, respectively.

The volume of the gas-manipulation line V_L was determined to be 102.076 ± 0.050 cm^{-3}, from five determinations by expansion of nitrogen from the line to the reference volume vessel. Since a temperature gradient is present along the reaction vessels and inlet tubes, the effective total volume V_{app} is calculated from eqns. (3) and (4) at various temperatures and pressures for the part below stop-cock 3 (shown in Fig. 1), by assuming that the whole part is at a temperature T. The part is divided into N equal volumes. Let T_i be the temperature at the ith volume. Then, V_{app} is related to the genuine volume V by the equation

$$V_{app} = V \sum_{i=1}^{N} [(T/T_i)Z(p,T)/Z(p,T_i)] \tag{5}$$

where V is the total volume of the part and T is the temperature of the reaction vessels. V_{app} was substituted into eqn. (3) together with T and p to calculate n(vessels).

Prior to calorimetric experiment, ammonia was admitted from the gas-manipulation line to the empty vessels to determine V_{app}. As shown in Fig. 3(a), pressure decreased gradually even after 24 h from the admission. The pressure decrease leads to the increase in apparent volume V_{app} with time as shown in Fig. 3(b). The increase in V_{app} was found to be expressed as the linear equation of $t^{1/2}$, where t is the time after admission of ammonia. $V_{app}(t)$ was found to agree within 0.6% for duplicate experiments. $V_{app}(t)$ curves for blank experiments were taken to reflect the decrease in ammonia

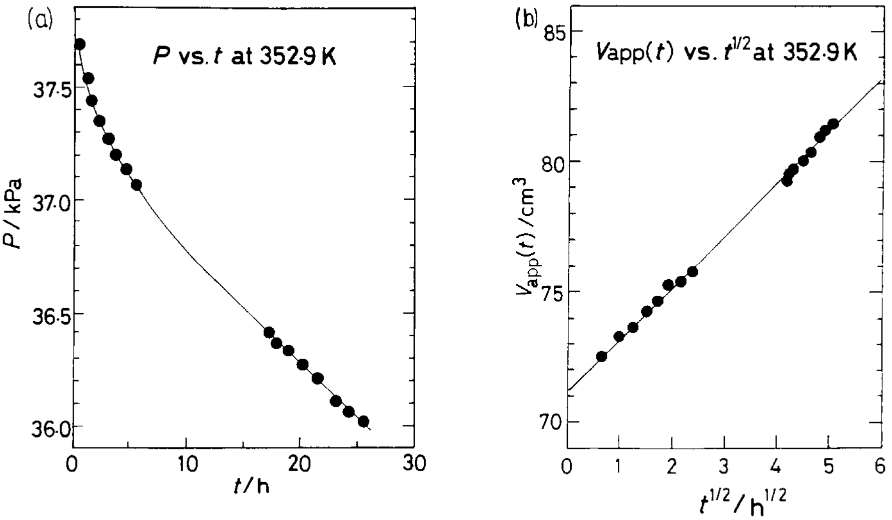

Fig. 3. (a) Gradual decrease in pressure of ammonia in the gas-manipulation section after the admission. (b) $V_{app}(t)$ vs. $t^{1/2}$ plots calculated from the p vs. t plots.

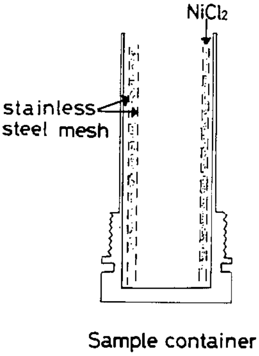

Fig. 4. The arrangement of the sample in the reaction vessel.

by some subsidiary causes. In the present test calorimetric experiments, V_{app} was evaluated after an experiment as the value of V_{app} at the same t read from the $V_{app}(t)$ curve of a blank experiment at a similar pressure and the same temperature. Since the contribution of n(vessels) to $n(NH_3)$ is between 30% and 50% of the total, the effect of the imprecision in $V_{app}(t)$ to $n(NH_3)$ is between 0.2% and 0.3%. $V_{app}(t)$ depends upon both temperature and pressure. The former was automatically taken into account by preliminary expansion of ammonia into empty vessels at the temperature at which calorimetric experiments are carried out. The latter dependence was shown by the fact that $V_{app}(t)$ at 36.5 kPa is 2.5% higher than the corresponding $V_{app}(t)$ at 75.5 kPa at 352 K. In the calorimetric experiments, the difference in pressure between a preliminary experiment for the determination of $V_{app}(t)$ and a subsequent calorimetric experiment was less than 3 kPa. Hence, by considering the contribution of n(vessels) to $-\Delta_r n$, the effect of the pressure difference to $\Delta_r n$ is within 0.1% of the total.

Nickel dichloride (40–77 mg) was sandwiched between two pieces of fine stainless steel mesh, which were rolled and placed along the internal surface of the active reaction vessel as shown in Fig. 4. Two pieces of mesh without nickel dichloride were placed in the same way in the reference reaction vessel. The arrangement was adopted so as to facilitate the conduction of reaction heat in the active reaction vessel. The charged active reaction vessel was evacuated at 353 K for 8 h, and then mounted in the calorimeter, together with the reference reaction vessel.

Prior to calorimetric experiments, the vessels and the gas-manipulation line were evacuated to 10^{-4} Pa, then the latter was filled with ammonia in excess of the amount necessary to ammoniate charged nickel dichloride completely. After the amount of ammonia in the gas-manipulation line was determined, the gas was admitted to the reaction vessels to start the reaction.

The area S_r (due to the reaction) in the calorimeter output voltage plot (Fig. 5) was evaluated by drawing a straight baseline which connects the

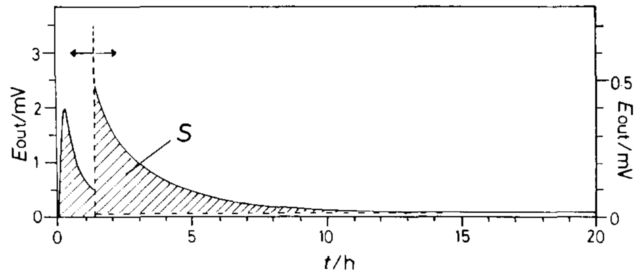

Fig. 5. Calorimeter output voltage (E_{out}) vs. time curve. Shaded area S corresponds to heat released during the reaction.

values at the start and at the end of the reaction. The heat absorbed Q was calculated by the equation

$$Q = -\varepsilon_a S_r \tag{6}$$

where ε_a is the energy equivalent (in J V^{-1} s^{-1}) of the active reaction vessel, which was determined by subsequent calibration experiments using a measured amount of electric energy. Initially, the electrical calibration experiments were carried out in situ using the built-in heater shown in Fig. 6. However, the mean of the derived standard enthalpy changes for reaction (1) at 298.15 K was found to be 2.5% higher than the calculated value based on the standard enthalpies of formation given in the literature [23]. As reported elsewhere [26], the standard enthalpy of formation of $[Ni(NH_3)_6]Cl_2$ at 298.15 K, based on separate solution-reaction calorimetric experiments, agreed with the literature value. A new series of electrical calibration experiments were performed for the gas–solid reaction apparatus using another electric heater (400 Ω) immersed in silicone oil and placed in the sample container. Derived energy equivalents were compared with those obtained by the in situ calibration experiments using the built-in heater. As shown in Table 1, energy equivalents obtained using the new method are systematically lower than the corresponding initial values. The ratio γ ($\equiv \varepsilon_a'/\varepsilon_a$) is nearly independent of temperature for each of the reaction vessels, and in the subsequent gas–solid reaction calorimetric experiment, the true energy equivalent of the active side was determined by correcting the value obtained using the built-in heater with the mean value (0.9751) of the correction factors at every temperature

$$Q = -\gamma \varepsilon_a S_r \tag{7}$$

Since the volume of sample charged in the active reaction vessel was less than 0.02 cm^3 in the present study, the contribution of the $V\Delta p$ term [27,28] to the total heat measured was less than 0.1% and was neglected. Hence, the

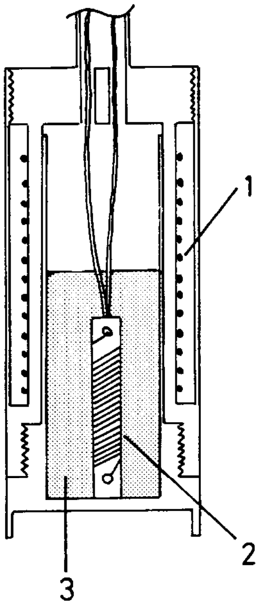

Fig. 6. Location of calibration heaters: 1, build-in heater (521.4 Ω); 2, the new heater (402.4 Ω); 3, oil.

standard enthalpy change was calculated as follows

$$\Delta_r \overline{H}^\ominus(T) = \frac{6Q}{n(NH_3)} \tag{8}$$

where $n(NH_3)$ is the amount of ammonia reacted, which was determined volumetrically.

The reaction was conducted at 353 and 360 K. Usually, 18–24 h were required for completion of reaction. When the change in area, as a result of the reaction (after the elapse of an additional 2 h) was less than 0.1% of the total, the reaction was judged to be complete. Then, the amount of gas left in the gas-manipulation line and in the inlet tubes and reaction vessels was determined volumetrically and the amount of gas reacted was calculated. The amount of gas reacted was also determined from the difference in weight of the active reaction vessel before and after the reaction.

Drop Calorimetry

To reduce the measured standard enthalpy changes of reaction (1) to the value at 298.15 K, the enthalpy change of $[Ni(NH_3)_6]Cl_2$(cr) on going from a temperature at which gas–solid reaction calorimetry was carried out to 298.15 K was measured by the temperature-jump (drop) calorimetric method, using another Tian–Calvet microcalorimeter (Setaram, ambient to 473 K type). In these experiments, pelleted $[Ni(NH_3)_6]Cl_2$ (cr) (0.36579 g), charged

TABLE 1

Energy equivalents of the gas–solid reaction system.

T(K)	ε_a(J V^{-1} s^{-1})	ε'_a(J V^{-1} s^{-1})	$\varepsilon'_a/\varepsilon_a$
272.66	16.849 ± 0.008(3)	16.422 ± 0.001(3)	0.9747 ± 0.0005
284.97	16.745 ± 0.005(4)	16.345 ± 0.010(4)	0.9761 ± 0.0007
349.64	16.666 ± 0.002(3)	16.225 ± 0.007(3)	0.9753 ± 0.0005
360.50	16.719 ± 0.004(3)	16.301 ± 0.004(3)	0.9750 ± 0.0003
		Weighted mean and twice sdm:	0.9751 ± 0.0001
T(K)	ε_r(J V^{-1} s^{-1})	ε'_r(J V^{-1} s^{-1})	$\varepsilon'_r/\varepsilon_r$
272.66	16.088 ± 0.070(2)	15.614 ± 0.002(2)	0.9705 ± 0.0042
284.97	16.051 ± 0.003(2)	15.558 ± 0.007(2)	0.9693 ± 0.0005
349.64	16.117 ± 0.002(2)	15.631 ± 0.005(2)	0.9698 ± 0.0003
360.50	16.184 ± 0.001(2)	15.685 ± 0.001(2)	0.9692 ± 0.0003
		Weighted mean and twice sdm:	0.9697 ± 0.0014

ε and ε' are the observed energy equivalents determined using the built-in heater and a second heater immersed in oil and placed in the sample container, respectively. Subscripts a and r denote the active and reference sides, respectively. The number of experiments is given in parentheses. Uncertainties are twice the standard deviation of the meant (sdm).

in a stainless-steel container, was transferred rapidly from a thermostat at 352 K or 360 K to a receiver placed in the active calorimetric well at 298.15 K. Simultaneously, an empty container of similar size was dropped to a receiver in the reference well. Subsequently, electrical calibration was carried out in situ. The effect of the heat capacity difference between the empty containers was accounted for [29].

RESULTS AND DISCUSSION

Gas–solid reaction calorimetry

The results are summarized in Table 2. Mean and standard deviation of the mean of the observed ratios $\{n(\mathrm{NH_3})/n(\mathrm{NiCl_2})\}$ were calculated as 6.004 ± 0.007 and 5.986 ± 0.024 using the volumetric and gravimetric methods, respectively. Both values agree with the theoretical value of 6.000 within the limits of uncertainty. The reaction is considered to be close to completion in every experiment. Since the volumetric molar ratio is more precisely determined, standard enthalpies of reaction at the calorimetric temperatures were based on the volumetrically determined amount of ammonia reacted.

The results of the temperature jump (drop) calorimetry of [Ni-

$(NH_3)_6]Cl_2$(cr) are given in Table 3. The enthalpy difference was derived by the equation

$$H^{\ominus}(T) - H^{\ominus}(298.15\ K) = \frac{-(Q+\delta Q)}{n([\mathrm{Ni(NH_3)_6}]\mathrm{Cl_2})} + \delta H_1 \qquad (9)$$

where $-Q$ is the heat released, $-\delta Q$ is the correction which accounts for the mismatch in the heat capacity of the vessels and in the sensitivity of the combined vessel-thermopiles, and $\delta H_1 = H^{\ominus}(T_1) - H^{\ominus}(298.15\ \mathrm{K})$. The derived results are expressed by the equation

$$H^{\ominus}(T) - H^{\ominus}(298.15\ \mathrm{K}) = -36.74 + 0.15446T \qquad (10)$$

The uncertainties at the 95% confidence level were 0.74 kJ mol^{-1} at 352.9 and 360.1 K.

Comparison with the literature value

$\Delta_r H^{\ominus}(T)$ values given in Table 2 were reduced to those at 298.15 K using the literature data of $H^{\ominus}(T) - H^{\ominus}(298.15\ \mathrm{K})$ for NH_3(g) and $NiCl_2$(cr) [30] and the present experimental data for $[Ni(NH_3)_6]Cl_2$(cr). The derived values are given in Table 2. The mean ± twice the overall standard deviation of the mean of the standard enthalpy change at 298.15 K for reaction (1) is -412.9 ± 1.9 kJ mol^{-1}. The $\Delta_r H^{\ominus}(298.15\ \mathrm{K})$ value based on the amount of nickel dichloride is -413.2 ± 1.9 kJ mol^{-1}, which agrees with the above-mentioned value. Both of these are in good agreement with the value -412.2 ± 1.4 kJ mol^{-1}, which is based on the literature data [23] of standard enthalpies of formation for compounds which appear in eqn. (1).

Problems associated with the present gas–solid reaction calorimetry

Location of calibration heater

The importance of this problem has been indicated by several authors [31,32]. In this study the ratio of the undetected to detected heat in the reaction calorimetry experiment was not identical with that in the calibration experiment using the built-in heater. The use of an additional heater immersed in oil and placed in the sample container improved the situation and a satisfactory result was obtained.

Determination of amount of gas

Significant adsorption on solids [33] has been reported for ammonia at ambient temperatures. However, the duration of the observed pressure decrease was so long that it cannot be explained solely by the adsorption. The absorption of ammonia into the grease at the joints and into the rubber O-rings used to seal the reaction vessels is suspected. The effect of the latter on the calorimetric output voltage would be largely canceled by virtue of the

TABLE 2

Summary of results of gas–solid reaction calorimetry

T (K)	$n(\mathrm{NiCl_2})$ (mmol)	Gravimetric		Volumetric				
		$n(\mathrm{NH_3})$ (mmol)	$\dfrac{n(\mathrm{NH_3})}{n(\mathrm{NiCl_2})}$	$n(\mathrm{NH_3})$ (mmol)	$\dfrac{n(\mathrm{NH_3})}{n(\mathrm{NiCl_2})}$	$-Q$ (J)	$-\Delta_r\overline{H}^\ominus(T)$ (kJ mol^{-1})	$-\Delta_r\overline{H}^\ominus(298.15\ \mathrm{K})$ (kJ mol^{-1})
352.84	0.3639	2.175	5.971	2.188	6.013	150.75	413.4	415.4
352.87	0.3499	2.090	5.973	2.107	6.022	144.19	410.6	412.6
352.90	0.3062	1.814	5.924	1.834	5.990	125.45	410.4	412.5
360.03	0.4557	2.768	6.074	2.740	6.013	186.91	409.3	411.9
360.20	0.5952	3.565	5.990	3.561	5.983	242.92	409.3	412.0
			Mean: 5.986		Mean: 6.004			Mean: 412.9
			sdm: 0.024		sdm: 0.007			sdm: 0.7

$n(\mathrm{NiCl_2})$, amount of $\mathrm{NiCl_2}$ placed in the reaction vessel; $n(\mathrm{NH_3})$, amount of $\mathrm{NH_3}$ reacted; $-Q$, heat released during the reaction; $\Delta_r\overline{H}^\ominus(T = 6Q/[n(\mathrm{NH_3})]$ and $\Delta_r\overline{H}^\ominus(298.15\ \mathrm{K})$ refer to reaction (1); sdm, standard deviation of mean.

TABLE 3

Relative enthalpies of $[Ni(NH_3)_6]Cl_2(cr)$

T_1 (K)	T (K)	$-Q$ (J)	$-\delta Q$ (J)	$[H^\ominus(T) - H^\ominus(T_1)]$ (kJ mol^{-1})	δH_1 J mol^{-1}	$[H^\ominus(T) - H^\ominus$(298.15 K)] (kJ mol^{-1})
298.17	350.96	24.15	3.95	17.80	6	17.81
298.18	350.80	22.60	3.94	16.81	9	16.82
298.18	350.78	23.86	3.93	17.61	9	17.62
298.32	350.87	24.08	3.93	17.75	52	17.80
298.20	350.87	22.90	3.94	17.10	15	17.12
298.26	350.78	23.66	3.93	17.48	34	17.51
298.09	350.14	23.73	3.93	17.53	−18	17.51
298.16	361.52	29.31	4.74	19.06	3	19.06
298.35	361.53	29.12	4.74	18.93	62	18.99
298.15	361.85	29.78	4.76	19.36	0	19.36
298.09	361.97	29.18	4.77	18.98	−18	18.96
298.35	362.35	29.68	4.80	19.29	62	19.35

$-Q$, heat released; δQ, heat due to mismatch in heat capacity of the vessels and in the effective sensitivity of the combined vessel-thermopiles; $\delta H_1 = H^\ominus(T_1) - H^\ominus(298.15\ \mathrm{K})$.

twin arrangement. In subsequent gas–solid reaction experiments using the same apparatus and oxygen, no such anomalous decrease in pressure for a long period was observed and the amount of gas was determined properly.

Thermal effect of gas adsorption onto the internal wall

This effect is considered to be largely canceled by the twin arrangement of the calorimeter and the reaction vessels.

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