Thermochemical energy calculations for the formation of aluminium by the Hall-Heroult-process

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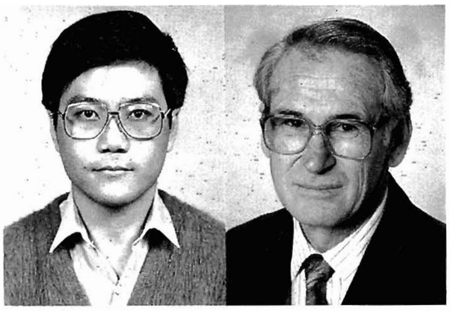

Knacke's method of thermochemical energy calculation for the aluminium electrolysis process is deficient. His calculation was based on an inappropriate and inconsistent stoichiometric equation, and significant energy terms were left out. This note illustrates that it is simpler to carry out the energy balance by first considering the reaction to occur at the reference temperature, followed by heating the products to reaction temperature.

Thermochemische Energiekalkulationen für die Bildung von Aluminium im Hall-Heroult-Prozeß

Die thermochemische Energiekalkulation für den Aluminium-Elektrolyseprozeß nach *Knacke* ist fehlerhaft. Seine Kalkulation basiert auf einer ungeeigneten und widersprüchlichen stöchiometrischen Gleichung, signifikante Energiebedingungen sind nicht beachtet worden. Dieser Beitrag zeigt auf, daß es einfacher ist, die Energiebalance dadurch zu erreichen, daß man zuerst die Reaktion beachtet, die bei der Referenz-Temperatur auftritt, gefolgt von einem Aufheizen des Produkts bis zur Reaktionstemperatur.

Calcul d'énergie thermochimique quant à la formation d'aluminium dans le procédé de Hall-Heroult

Los cálculos de energía termoquímica para la formación de aluminio en el procedemiento Hall-Heroult

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Grjotheim et al. [1] refer to an alternative energy balance for aluminium electrolysis by *Knacke* [2] based on "a direct balance of the temperature – dependent enthalpies of the participating substances". *Knacke* [2] based his calculations on a particular operating condition given by *Schmidt-Hatting* [3] which has an anode consumption rate of 500 g/kg Al, alumina consumption rate of 1890 g/kg Al, bath temperature of 960 °C, cell voltage of 4.14 volts and a current efficiency (x) = 0.895. The material balance and standard molar enthalpies were listed (Tab. 1).

Based on Table 1, the following stoichiometric equation was given:

$$1/2\ Al_2O_3\ (25°) + 1.123\ C\ (25°) + 3.352\ e_{Al} \rightarrow Al\ (960\ °C) + 0.746\ CO\ (25°) + 0.377\ CO_2\ (25°) + 3.352\ e_{CO,CO_2} \qquad (1)$$

In order to simplify the problem, *Knacke* [2] suggested that it "does not introduce a large error" by setting the exhaust gas temperature to 25 °C. The enthalpy change was obtained as follows:

Table 1. Material balance and standard molar enthalpies [2]

i	$\frac{i\ g}{kg\ Al}$	$\frac{i\ mol}{mol\ Al}$	Temp. °C	$H°_i\ (T)$ kJ/mol
C	500	1.123	25	0
Al_2O_3	1890	0.5	25	-1673.0
Al	1000	1	960	38.4
CO		0.746	25	-110.5
CO_2		0.377	25	-393.5
e^1		3.352		

[1] The number of electrons involved was obtained by dividing 3, the valence of aluminium, by 0.895, the current efficiency.

$$\Delta H° = \Sigma \nu_i H_i° (T_i) = 0.377 \text{ x } (-393.5) + 0.746 (-110.5) + 38.4 - 0.5 (-1673.0) = 644 \text{ kJ/mol Al}$$

There is, however, an internal inconsistency in Eq. (1). While the number of electrons transferred was set by the current efficiency value of 0.895 i.e. valence = 3 for Al and divided by 0.895, the coefficients for C, CO and CO_2 require some other current efficiency. The stoichiometric coefficient for carbon was derived from the operating data given in Table 1 which includes airburn contribution. Although some electrochemical evolution of carbon monoxide is known to occur on the sides of the anode, this is dependent on carbon quality and operating current density. Thus, not all the carbon is involved in the electrochemical process. While the excess carbon is mostly combusted in the cell, it does not occur in the electrolyte and will not contribute towards the heat content of the bath. Moreover, the workings presented appear to have omitted certain significant enthalpy terms.

The electrolytic reaction may be written as

$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2 \tag{2}$$

The back reaction which contributes to the loss in current efficiency, is given by

$$2Al + 3CO_2 \rightarrow Al_2O_3 + 3CO \tag{3}$$

Combining Eqs. (2) and (3) by assuming y times of reaction (3) had occurred and re-arranging.

$$2Al_2O_3 + 3C \rightarrow (4\text{-}2y)Al + (3\text{-}3y)CO_2 + yAl_2O_3 + 3yCO \tag{4}$$

The current efficiency, x, may then be written as

$$x = \frac{4-2y}{4} = 1 - \frac{y}{2} \tag{5}$$

The ratio fo the volumes of CO to CO_2 produced $[CO]/[CO_2]$ may be written as

$$\frac{[CO]}{[CO_2]} = \frac{3y}{3-3y} = \frac{y}{1-y} \tag{6}$$

If only CO and CO_2 are produced

$$\frac{1-[CO_2]}{[CO_2]} = \frac{y}{1-y} \tag{7}$$

It may then be readily shown that

$$y = 1 - [CO_2] \tag{8}$$

Substitution of Eq. (8) into Eq. (5) gives

$$x = 1 - \frac{1-[CO_2]}{2} = 1/2 + \frac{[CO_2]}{2} \tag{9}$$

which is the *Pearson-Waddington* equation.

Eq. (4) may be re-written as

$$\left[\frac{2-y}{4-2y}\right] Al_2O_3 + \left[\frac{3}{4-2y}\right] C \rightarrow Al + \left[\frac{3-3y}{4-2y}\right] CO_2 + \left[\frac{3y}{4-2y}\right] CO \tag{10}$$

Eliminating y using Eq. (5) results in

$$1/2\ Al_2O_3 + \frac{3}{4x}C \rightarrow Al + \frac{3}{4}\left(2-\frac{1}{x}\right) CO_2 + \frac{3}{2}\left(\frac{1}{x}-1\right) (\tag{11}$$

which is the same as that given by *Grjotheim* et al. [1].

Thus, comparing Eq. (1) with Eq. (11) requires a current efficiency *CE* of 0.668 as compared to the given value of 0.895, a major inconsistency in Eq. (1) as treated by *Knacke* [2].

To offer a direct comparison of the results due to *Knacke* [2] with the conventional method as given by *Grjotheim* et al. [1], the following calculations will be conducted, based on a 100% current efficiency for simplicity:

$$1/2\ Al_2O_3 + 3/4\ C \rightarrow Al + 3/4\ CO_2 \tag{12}$$

Accordingly Table 2 for 1250 K was prepared. The values for $H°_T - H°_{298}$ are for 1250 K (977 °C) and obtained from the JANAF Tables [4] so as to allow direct comparison with the results given by *Grjotheim* et al. [1]. The values for $\Delta_f H°$ are those for the reference conditions of 25 °C. It is noted that $\Delta_f H°$ for Al is given as zero while *Knacke* [2] gave this value as 38.4 kg/mol at 960 °C as indicated by the values in brackets in Table 2. Using *Knacke's* method,

$$\Delta H°_{Knacke} = 0.75\ (-393.522) + 38.4 - 0.5\ (-1675.692) = 581\ \text{kJ/mol} = 5.98\ \text{kWh/kg Al} \tag{13}$$

In the conventional method of calculation, there are two alternative routes for the calculation of the enthalpy requirement. The first alternative assumes that the reaction takes place at the reference temperature (25 °C), followed by heating the products to the reacting temperature. Thus, the total enthalpy $\Delta H°_{Total}$ is

$$\Delta H°_{Total} = \Delta_f H°_{298} + \Sigma_{products,T}\,(H°_T - H°_{298}) \tag{14}$$

The second alternative assumes that the reactants are first heated to the reaction temperature T and subsequently allowing the reaction to occur at the new temperature T. The heat of reaction at the new temperature T is given by

$$\Delta_f H°_T - \Delta_f H°_{298} = \Sigma_{products,T}\,(H°_T - H°_{298}) - \Sigma_{Reaetants,T}\,(H°_T - H°_{298}) \tag{15}$$

It is clear that when the heat required to raise the reactants to the reacting temperature T is added to $\Delta_f H°_T$ as given in Eq. (15), Eq. (14) will be obtained. Thus, it is sufficient to consider only Eq. (14) which, when applied to the data given in Table 2 gives

$$\Delta_f H°_{298} = 0.75\ (-393.522) - 0.5\ (-1675.692) = 542.705\ \text{kJ/mol}$$

$$\Sigma_{product,T}\,(H°_T - H°_{298}) = 0.75\ (47.311) + 38.744 = 74.227\ \text{kJ/mol}$$

Thus,

$$\Delta H°_{Total} = 617\ \text{kJ/mol} \equiv \mathbf{6.347\ kWh/kg\ Al} \tag{16}$$

Table 2. Material balance and enthalpies for Eq. (12)

Component	mol/mol Al	Temp. °C	$\Delta_f H°_{298}$ kJ/mol	$H°_{1250} - H°_{298}$ kJ/mol
C	0.75	25	0	Not needed
Al_2O_3	0.5	25	-1675.692	Not needed
Al	1	25 (960)	0 (38.4)	38.744
CO_2	0.75	25	-393.522	47.311

M.P. Taylor obtained his PhD in 1984 at the University of Auckland where he studied heat transfer processes in aluminium smelting under the supervision of Professor B. Welch. Since then he has worked at the Comalco Research Centre on various aspects of the smelting process, including a number of computer modelling investigations. Currently Dr. Taylor is Principal Research Scientist in the Reduction Group at Comalco Research. He has authored 25 publications on aluminium smelting and in 1990 was awarded the Esso Award for Excellence in Chemical Engineering.

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This result is in agreement with *Grjotheim* et al. [1], but *Knacke's* [2] method gave a lower value of 5.98 kWh/kg (13).

It appears by comparing Table 1 with Table 2 that *Knacke* [2] has allowed for the heat required for heating the aluminium to the reacting temperature by putting $H^\circ_i(T)$ = 38.4 kJ/mol. However, the standard enthalpy changes for CO and CO_2 were not allowed for.

A revised calculation for the situation given by *Knacke* [2] for 960 °C will be performed using Eq. (14) based on the revised data shown in Table 3. Applying Eq. (14) gives

$$\Delta H^\circ_{\text{Total}} = [0.377\,(-393.522) + 0.746\,(-110.527) - 0.5\,(-1675.692)] + [0.377 \times 46.346 + 0.746 \times 29.565 + 38.204] = 685\ \text{kJ/mol} \equiv \mathbf{7.05\ kWh/kg\ Al}$$

Thus, the total energy demand for the situation as considered by *Knacke* is 7.05 kWh/kg Al as opposed to the value of 6.63 kWh/kg Al reported by *Knacke*.

Table 3. Revised data for *Knacke's* sample calculations [1]

Component	mol/mol Al	$\Delta_f H^\circ_{298}$ kJ/mol	$H^\circ_{1233} - H^\circ_{298}$ kJ/mol
C	1.123	0	Not needed
Al_2O_3	0.5	-1675.692	Not needed
Al	1	0	38.204
CO	0.746	-110.527	29.565
CO_2	0.377	-393.522	46.346

In conclusion, *Knacke's* method of calculating the standard enthalpy change has omitted a number of significant components. Furthermore, the basis of his calculations is faulty as the number of electron transfers considered was inconsistent and the amount of carbon considered included that consumed outside of the electrochemical process (and outside of the electrolyte).

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