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Joseph William Richards

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## THE ROLE OF FORMATION HEATS OF ALLOYS IN ELECTROLYSIS.

BY JOSEPH W. RICHARDS.

The abstract in the November number of *ELECTROCHEMICAL INDUSTRY*, page 547, of the article in the *Journal de Chimie Physique*, by Lonquinine and Schukareff concerning the heat of formation of copper-aluminium alloys, gives rise to the query as to how these values should be utilized by the electrochemist in his calculations of the work done by the current in forming or decomposing alloys.

The values given by Lonquinine and Schukareff are the gram calories evolved in the formation of a gram of each alloy. The first five are exothermic, the last endothermic. (In the abstract, the minus sign was omitted from the last value, — 57.2, and the abstractor was wrong in his presumption that the values given were the kilogram calories per gram molecular weight of alloy formed.)

The correct data, and their derived values, which serve as the starting point for any electrochemical calculations, are as follows:

Formula.	Heats of Formation.			
	Per Cent of Al.	Per Molecular Weights.	Per Gram of Alloy.	Per Molecular Weight in Grams.
Cu <sub>3</sub> Al .....	12.5	217.9	123.5	26,910
Cu <sub>2</sub> Al .....	17.6	154.3	137.9	21,278
Cu <sub>3</sub> Al <sub>2</sub> .....	22.1	245.0	71.0	17,395
Cu Al .....	29.9	90.7	20.8	1,887
Cu <sub>2</sub> Al <sub>3</sub> .....	39.0	208.5	48.9	10,196
Cu Al <sub>2</sub> .....	46.0	117.8	— 57.2	— 6,738

None of these quantities, however, are directly applicable to electrochemical calculations, because they do not concern the chemical equivalent weights (deposited by 96,540 coulombs) of the aluminium, or copper, or alloy concerned. The copper may be in or pass into the electrolyte as a monad or dyad, the aluminium as a triad. Therefore, the formula of each alloy may represent, electrolytically, the following number of equivalents of the respective elements:

Formula	Cu <sub>x</sub> <sup>·</sup>	Cu <sub>x</sub> <sup>··</sup>	Al <sub>y</sub> <sup>···</sup>	Cu <sub>x</sub> +Al <sub>y</sub> <sup>···</sup>	Cu <sub>x</sub> +Al <sub>y</sub> <sup>···</sup>
Cu <sub>3</sub> Al	6	3	3	9	6
Cu <sub>2</sub> Al	4	2	3	7	5
Cu <sub>3</sub> Al <sub>2</sub>	6	3	6	12	9
Cu Al	2	1	3	5	4
Cu <sub>2</sub> Al <sub>3</sub>	4	2	9	13	11
Cu Al <sub>2</sub>	2	1	6	8	7

It follows from this, that the calories concerned in the solution or deposition of one of the above alloys, reckoned per 96,540 coulombs of current flowing, or one chemical equivalent concerned, varies, according to which ingredient of the alloy is the one dissolved or deposited, or whether the alloy, as a whole, is dissolved or deposited. The quantity required may be obtained by dividing the molecular heats of formation by the chemical equivalents concerned, as classified in the preceding table. We thus obtain the following table of heats *absorbed*, let us say, per 96,540 coulombs passing, under each of the five possible cases already classified, when the alloys are corroded:

I. When Cu only is dissolved, going into solution as cuprous salt.

II. When Cu only is dissolved, going into solution as cupric salt.

III. When Al only is dissolved.

IV. When the whole alloy is dissolved, the Cu dissolving as cuprous salt.

V. When the whole alloy is dissolved, the Cu dissolving as cupric salt.

Alloy attacked.	I.	II.	III.	IV.	V.
Cu <sub>3</sub> Al	4,485	8,970	8,970	2,990	4,485
Cu <sub>2</sub> Al	5,320	10,640	7,093	3,040	4,258
Cu <sub>3</sub> Al <sub>2</sub>	2,900	5,800	2,900	1,450	1,835
Cu Al	943	1,887	629	377	472
Cu <sub>2</sub> Al <sub>3</sub>	2,549	5,098	1,133	784	927
Cu Al <sub>2</sub>	— 3,369	— 6,738	— 1,123	— 842	— 963

It will be noted that the heat absorbed in the decomposition of the last alloy is negative, i. e., heat is evolved in its decomposition. The above values are heats absorbed in the corrosion and decomposition of the alloys. For formation of the alloys, heat will be evolved, according to the values of the above table, according to the ingredient which is deposited from the electrolyte.

All these heats, as given above, are directly convertible into voltage generated or absorbed, by dividing by the thermochemical equivalent of one volt, viz. 23,040 calories.

The principles involved in the above calculations are directly applicable to all cases of formation or decomposition, electrolytically, of alloys in general, including amalgams. The principle is well known where only one ingredient is deposited or dissolved, as in the formation and decomposition of sodium amalgam, but the above calculations cover the case also of *both* ingredients being simultaneously deposited or dissolved.

Metallurgical Laboratory,  
Lehigh University.