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VARIATION IN THE FREE ENERGY AND HEAT CONTENT IN REACTIONS LEADING TO THE FORMATION OF COBALT ARSENIDES

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Introduction

As a result of research on the dissociation pressures of cobalt arsenides (1), it was found that the dissociation proceeds gradually. The end results of the dissociation reactions can be seen from the following equations (s = solid, g = gaseous):

$$8CoAs_2(s) = 4Co_2As_3(s) + As_4(g);$$
$$4Co_2As_3(s) = 8CoAs(s) + As_4(g);$$
$$12CoAs(s) = 4Co_3As_2(s) + As_4(g);$$
$$8Co_3As_2(s) = 12Co_2As(s) + As_4(g);$$
$$20Co_2As(s) = 8Co_5As_2(s) + As_4(g);$$
$$2Co_5As_2(s) = 10Co(s) + As_4(g).$$

Investigation of the dissociation pressures of cobalt arsenides was dictated by the necessity of studying in detail the oxidation-reduction reactions taking place in pyrometallurgy.

Results of determining the dissociation pressures, notwithstanding the observed narrow temperature intervals with anomalous values close to the critical points (1), demonstrate in several ranges of temperature, a uniformity in their changes; and also permit the determination of the change in free energy and the heat content resulting from the formation of the compounds.

From a practical point of view, the intervals in temperature during which the reactions with the arsenides proceed intensively, particularly those during heating at temperatures close to the temperature of ignition in air and at the melting point, are of great interest.

Temperatures of ignition of cobalt arsenides and the dissociation pressures at temperatures close to them are as follows:

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ARMY	X	AIR	X	FBI							

Table I

Arsenides	Ignition Temp, in Deg C (class 0.138+0.06? mm)	Dissociation Pressures: P_{As_4} (in mm mercury)	Dissociation Pressures: Correspondent Temp
$CoAs_2$	540	$3.8 \cdot 10^{-3}$	542
Co_2As_3	610	$1.45 \cdot 10^{-3}$	615
$CoAs$	775	$7.21 \cdot 10^{-5}$	768
Co_3As_2	785	$6.97 \cdot 10^{-5}$	778
Co_2As	790	$5.32 \cdot 10^{-5}$	787
Co_5As_2	805	$5.61 \cdot 10^{-5}$	798

According to research by Preyner and Brokmoler (2), at temperatures of 800-900 degrees centigrade and pressure of 750 millimeters, the molecules of gaseous arsenic are 94 percent tetratomic. With the lowering of the pressure to 10^{-4}--10^{-5} mm, further dissociation into diatomic molecules occurs; but for the purposes of calculation, it is sufficient to assume that the molecules of gaseous arsenic in all cases are tetratomic.

Since the dissociation pressures of the cobalt arsenides are very small, it can be assumed that the vapors of arsenic comply with the ideal gas laws that all thermodynamic equations for ideal gases apply also to them (6).

Vapor pressures of arsenic gas, determined for the dissociation reactions of arsenides, represent constants of equilibrium of the six reactions for which the equations were previously given.

Therefore, the change in free energy ($\Delta\phi$) can be determined according to the equation for the isotherm of the reaction $\Delta\phi = -A = -RT \ln K_p$, and the change in heat content readily can be determined according to the equation for the isobar of the reaction

$$\ln \frac{K_2}{K_1} = \frac{\Delta H(T_2 - T_1)}{4.575\, T_1 T_2}$$

Summary of Results

The higher cobalt arsenides, as well as the monoarsenide, are found in nature in the form of minerals (scutterudite - $CoAs_3$; smaltine - $CoAs_2$; and moderite - CoAs) and also as components of other ores.

The changes in free energy and heat content resulting from the formation of cobalt arsenides from the two elements, calculated for 12 gram atoms of cobalt at 740 degrees centigrade and 1014 degrees centigrade (see tables below), increase in passing from the lower arsenides to the high .

Table 2. Change in Free Energy and Heat Content through Formation of Cobalt Arsenides from the Elements at 740 Centigrade (in calories)

Arsenides	Per 1 Gram Atom of the Compound		Per 1 Gram Atom of Co		Per 1 Gram Atom of As	
	$\Delta\phi$	ΔH	$\Delta\phi$	ΔH	$\Delta\phi$	ΔH
Co_5As_2	-18,765	-41,240	-3,753	-8,248	-9,303	-20,620
Co_2As	-9,336	-20,628	-4,668	-10,314	-9,336	-20,628
Co_3As_2	-18,345	-41,603	-6,115	-13,840	-9,173	-20,802
$CoAs$	-9,000	-20,790	-9,000	-20,790	-9,000	-20,790
Co_2As_3	-22,329	-58,248	-11,160	-29,124	-7,443	-19,416
$CoAs_2$	-12,205	-37,580	-12,205	-37,580	-6,102	-18,790

Table 3. Change in Free Energy and Heat Content Through Formation of Cobalt Arsenides From the Elements at 1014 Centigrade (in calories)

Arsenides	Per 1 Gram Atom of the Compound		Per 1 Gram Atom of Co		Per 1 Gram Atom of As	
	$\Delta\phi$	ΔH	$\Delta\phi$	ΔH	$\Delta\phi$	ΔH
Co_5As	-15,108	-36,610	-3,022	-7,322	-7,554	-18,305
Co_2As	-7,678	-18,246	-3,839	-9,132	-7,678	-18,264
Co_3As_2	-14,578	-38,436	-4,859	-12,812	-7,289	-19,218

Therefore, a general regularity in the changes of chemical affinity in the process of formation of several chemical compounds from the two elements can be observed.

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