

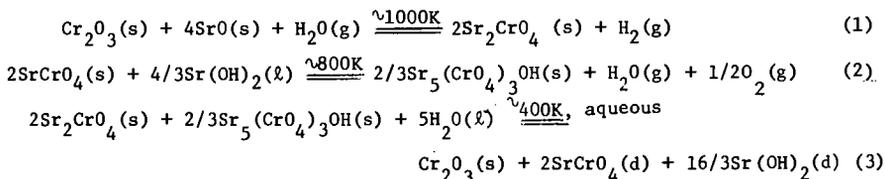
THERMOCHEMICAL DECOMPOSITION OF WATER BASED ON REACTIONS OF CHROMIUM AND STRONTIUM COMPOUNDS*

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The predictable future shortage of natural gas as a raw material for the production of hydrogen will require the use of water, an inexhaustible source. High efficiency decomposition of water may be attained by thermochemical cycles in which energy is expended primarily as heat. Although over seventy thermochemical cycles have been proposed⁽¹⁾ only a small fraction appears to merit further consideration. Continued research and investment will assure that the most efficient and practical cycles are developed. The chemistry of ternary oxides of chromium makes possible a closed cycle consisting of three reactions. One such cycle involving barium chromates (IV), (V) and (VI) has been described⁽²⁾. This paper reports a similar cycle of the strontium chromates (IV), (V) and (VI) that affords lower temperatures and easier separations than prevail in the barium cycle.

The proposed cycle consists of the following reactions:



where (d), (g), (ℓ) and (s) refer, respectively, to the states dissolved, gaseous, liquid and solid. The net reaction is H₂O decomposing to H₂ and 1/2O₂.

These reactions were experimentally confirmed in laboratory equipment at one atmosphere total pressure under flowing argon. According to published results⁽³⁾ Cr₂O₃ is not oxidized by Sr(OH)₂. Our work, however, showed partial reaction with 28% of expected hydrogen being evolved. Starting from ambient the temperature was continuously increased and maximum hydrogen pressure was observed at 800 C followed by rapid decline. This was to be expected since the dissociation pressure of H₂O over Sr(OH)₂ reaches 710 torr at 700 C⁽⁴⁾. The addition of LiOH as a flux and additional oxidant (hydroxyl ion) raised the hydrogen yield to 43%. Such additions, however, increase the corrosivity of the mixture and later separation problems would complicate the cycle. It was then demonstrated that the extent of reaction was dependent on the partial pressure of steam and independent of the ratio Sr/Cr. With steam pressure limited to approximately one atmosphere by the equipment used the maximum rate of hydrogen evolution occurred in the

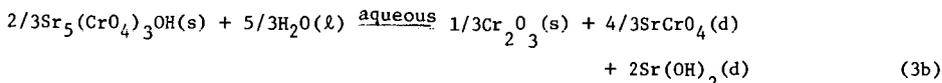
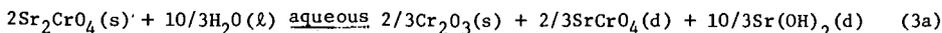
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vicinity of 700°C and 100% yield was obtained below 800°C. The product Sr_2CrO_4 was confirmed by chemical analysis and x-ray powder diffraction.

Reaction (2) was first established by Scholder and Suchy (5) who used a flowing atmosphere of moist nitrogen at 700-1000°C. They also found that the product, $\text{Sr}_5(\text{CrO}_4)_3\text{OH}$, was stable in dry nitrogen up to 850°C. In the present work it was found that a moist purge was not required because the reaction occurs at much lower temperatures, 480-580°C, at which the dissociation pressure of H_2O over $\text{Sr}(\text{OH})_2$ is not very large, ≤ 100 torr⁽⁴⁾. The reaction proceeded to completion with only a small excess of $\text{Sr}(\text{OH})_2$ over the required stoichiometric ratio; this was confirmed by measurement of O_2 evolved, by chemical analysis and by x-ray diffraction.

Definitive information was not available on the hydrolytic behavior of Sr_2CrO_4 and of $\text{Sr}_5(\text{CrO}_4)_3\text{OH}$. The former was reported less stable toward water than its barium analog (3,6). In relation to $\text{Sr}_5(\text{CrO}_4)_3\text{OH}$ it was reported that $\text{Ca}_5(\text{CrO}_4)_3\text{OH}$ is not stable in cold water (7) and that $\text{Ba}_5(\text{CrO}_4)_3\text{OH}$ undergoes hydrolytic disproportionation in hot water (2). Experimental determination of the hydrolysis of each compound was conducted in a Soxhlet extractor under argon. The results obtained are represented by the following reactions:



Since the same hydrolysis products are obtained both reactions can be combined as reaction (3).

The demonstration of reactions (1), (2) and (3) validates the cycle proposed in Fig. 1. The temperatures required have already been exceeded in High Temperature Gas (Cooled) Reactors, the number of reactions is the minimum required (8), and there are no difficult gas separation problems. The laboratory experiments were conducted with static reagents, thus on a dynamic engineering scale it may be expected that kinetics would be more favorable and that lower temperatures would be required. In comparing the Ba-Cr cycle described earlier (2) with the present Sr-Cr one, it is evident that the latter is more attractive on the basis of fewer separation problems and lower reaction temperatures. Although the solubility of SrCrO_4 is low, 4.47 mM/l at 25°C, it is about 400 times more soluble than BaCrO_4 (9); thus, we were able to separate SrCrO_4 completely from Cr_2O_3 . The subsequent separation of SrCrO_4 and $\text{Sr}(\text{OH})_2$ can be easily achieved because of their very different solubilities enhanced by the presence of the common ion Sr^{2+} .

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