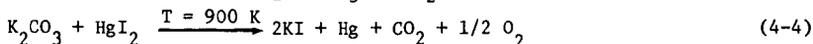
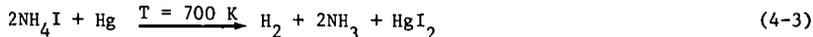
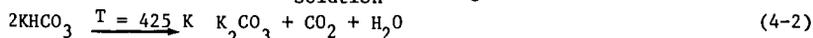
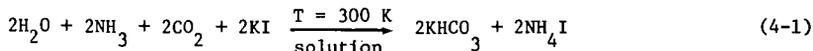


A PROMISING THERMOCHEMICAL CYCLE FOR SPLITTING WATER

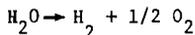
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The continued search at Argonne National Laboratory for a process by which water can be decomposed thermochemically has led to the development of a reaction sequence that requires a maximum temperature no higher than 900 K. The cycle has been designated ANL-4 and consists of the following reactions:



The sum of reactions (4-1) - (4-4) is the splitting of one mole of liquid H_2O



The thermodynamic analysis of this scheme shows it as potentially being capable of converting nearly 60% of the high-temperature heat into chemical potential energy, and laboratory experimentation indicates favorable rates and yields for the important high-temperature reactions. The process flow diagram brings out the advantageous feature of the cycle that most of the reactants and products can be handled as gases, melts, or as solutions. There remain certain problem areas such as the comparatively low separation efficiency of reaction (4-1) which necessitates the recycling of relatively large volumes of solutions and the presence of mercury in the effluent gases from reaction (4-4).

These reactions require additional work; nonetheless, there is good reason to believe that further development will be successful in improving the cycle.

It has been shown previously that the principal thermodynamic characteristics of a cycle are conveniently represented by a diagram of entropy versus temperature (3). Such a diagram for the cycle ANL-4 is shown in Figure 1 which was constructed from the data listed in Table 1. For the most part the numbers were taken from tables of "Thermochemical Properties of Inorganic Substances" by Barin and Knacke(4). In the case of potassium hydrogen carbonate the required quantities were calculated from the dissociation pressure curve(5) or estimated by comparison with sodium hydrogen carbonate.

The closed-loop trace of the entropy-temperature diagram represents the entropy changes of reactants and products during traversal of the complete water decomposition cycle according to the reactions (4-1) through (4-4). In order to close the loop thereby indicating that the entire system has been returned to the initial physical state, the entropy of formation of liquid

water is included. The numerical values used in the drawing of Figure 1 refer to the splitting and recombination of one mole of water so that the area enclosed by the loop represents the Gibbs energy of formation for one mole of water at 298.15 K (237.2 kJ).

The sign of the entropy change for each reaction is indicated by the direction of the arrow. The temperatures at which the arrows for the respective reactions are plotted are the temperatures at which the Gibbs energies are zero, with the exception of the arrow representing the re-formation of water at 298.15 K.

Three of the reactions, (4-2), (4-3), and (4-4) absorb heat, which must be furnished from the primary source. The minimal thermodynamic heat requirement for this water decomposition cycle is 527 kJ. The efficiency of the cycle, in turn, is expressed in the usual manner by the ratio of the chemical potential energy, i.e., the Gibbs energy of formation of the water, to the heat requirement. For the cycle ANL-4 this ratio is $\eta_{ANL-4, ideal} = 0.45$. The temperature of the primary heat source furnishing the energy for the water splitting process must be high enough to permit the reaction (4-4) to proceed, that is to say it must be at least 810.8 K. A classical Carnot-type heat engine operating between this temperature and ambient would be capable of converting 63% of the heat into useful work.

Three of the reactions making up the water decomposition cycle ANL-4 were studied in the laboratory in order to check the general chemistry, to verify the results of the thermodynamic calculations, and to demonstrate adequacy of reaction rates. They include the reaction (4-1), and the two high-temperature reactions (4-3) and (4-4).

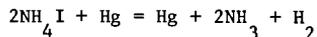
Reaction (4-1) involves the conversion of potassium iodide into potassium hydrogen carbonate in a solvent medium. Unfortunately, it is not possible to use water alone for the solvent as can be done so successfully in the case of sodium salts. However, with mixtures of organic solvents and water it is possible to achieve the conversion to an adequate extent. The data listed in Table 2 support this conclusion. They were obtained by heating equimolar mixtures of ammonium hydrogen carbonate and potassium iodide with the solvents to near boiling temperature, at which point the ammonium hydrogen carbonate is not stable. It was quickly established that the mixtures had to be pressurized either with mixtures of ammonia and carbon dioxide or with carbon dioxide alone, in order to improve the conversion efficiency. Samples from the saturated solutions were taken after equilibration and cooling to ambient temperature, and analyzed chemically.

The comparatively short series of experiments with a variety of solvent mixtures led to workable levels of salt interconversion with a 87.5% aqueous isopropanol solution under pressure of 50 psi of carbon dioxide.

The salt composition in that solution after equilibration corresponds to a mixture of 77% of ammonium iodide, 16% of potassium iodide, and of 7% of potassium hydrogen carbonate. It is very likely that still better systems can be found by further experimentation, but for the purpose of the present study the 7:1 isopropanol - water mixture was considered satisfactory.

The two high temperature reactions (4-3) and (4-4) were found to be straightforward and to proceed in accordance with the respective equations.

They are not encumbered by side reactions that lower product yields. It was also found that the equilibrium temperatures calculated from literature data are close to the observed values. Experimental results of the measurement of the reaction



are summarized in Table 3. These numbers were obtained by enclosing known quantities of ammonium iodide and mercury in a cylindrical reaction vessel made of fused silica. The vessel had a diameter of about 50 mm and a volume of approximately 300 cm³. It was loaded with the reactants, sealed under vacuum, then placed in a furnace and heated to the experimental temperature. After an equilibration time of up to one hour the vessel was removed from the furnace and cooled quickly. For analysis of the products, the vessel was attached to a pumping line by way of a breakseal. The gaseous products were separated by fractional condensation at 77 K and at 195 K (solid CO₂). The gases were transferred into known volumes with a Toepler pump and the pressure determined with a fused quartz Bourdon gage. To identify the products, samples were taken for mass-spectrometric analysis. The analysis showed the gases to have the composition expected from the equation; and no evidence for the decomposition of ammonia was found.

In addition to the measurement of equilibrium constants the rates of the reaction (4-3) were determined. In this case, the fused silica reaction vessel was equipped with optical windows which were recessed by approximately 5 cm in re-entrant wells at both ends. It was possible by this precaution to avoid condensation of mercury or mercury iodide vapor on the windows. The reaction rates at various temperatures were determined by following the build-up of mercuric iodide vapor photometrically. The reaction vessel was charged with a known quantity of NH₄I and a known quantity of Hg contained in an evacuated soft glass ampoule. The reaction was initiated at the experimental temperature by fusing the ampoule located in a side arm of the reaction vessel so the Hg vapor could contact the vaporized NH₄I

The observed rate at 680 K was proportional to the concentration of mercury and the concentration of ammonium iodide, and the second order rate constant has the value

$$k = 1.7 \pm 0.1_3 \text{ lit/s/mole.}$$

The half time for the reaction is $t_{1/2} = 2.3$ minutes at moderate experimental pressures of ~ 0.5 atm for the initial pressure of HI.

Measurements of equilibrium constants were also carried out for reaction (4-4). Rate measurements have not been made but qualitatively the reaction seems rapid. In this case, too, it was found that the calculated numbers agreed well with the experimental data. Since potassium carbonate at high temperatures attacks the fused silica, the solid reactants were contained in a magnesia crucible and the reaction vessel was mounted vertically.

A mixture of 2.2 mmol of HgI and 7.24 mmol of K₂CO₃ evolved 1.08 mmol of oxygen at 899 K; this corresponds to 98% reaction. The experimental K_p = 13.4 and the calculated K_p = 12.4.

The conclusions from the experimental investigation of the reaction of the cycle ANL-4 can be summarized as follows: All reactions can be carried out under conditions under which reasonably rapid rates are obtained and the yields of the high-temperature reactions are essentially 100%. The highest temperature required is 900 K. The chemistry of the reactions follows the equations (4-1) through (4-4) and there are no harmful side reactions. In particular, no decomposition of any of the ammonia was observed with reaction (4-3). With respect to yields, reaction (4-1) is the least attractive one, and since the overall solubility is not very high in the isopropanol mixture appreciable volumes of solution have to be cycled during the process. However, the solution need never be handled at very high temperatures, and waste heat from extraneous sources might be used to make up losses that cannot be recovered by a system of heat exchangers.

The movement of energy, reactants and products of the cycle ANL-4 are shown in the flow diagram Figure 2. There are, broadly speaking, three major sections in this diagram. On the left hand side there is a column representing from top to bottom the operations concerned with the recovery and calcination of potassium hydrogen carbonate and the subsequent reaction during which oxygen is released. A similar column on the right hand side shows the operations of recovering the ammonium iodide from solution and of producing the hydrogen in the reaction of NH_4I with mercury. Finally, surrounding the two vertical sections is a peripheral loop representing the circulation of solution or slurry.

Primary heat is furnished to the reactors at R42, R44, and R43 (a certain small fraction of heat, also indicated as stemming from the primary source, is used to dry the ammonium iodide). The water feed enters the process as make-up water in the scrubber which removes the ammonia from the product hydrogen. The ammoniacal solution containing a residual amount of iodide is moved clockwise into a second scrubber where it is pressurized with carbon dioxide at the same time that the oxygen leaves the process. Potassium iodide is added and the resultant slurry is heated to near boiling point temperature. The heating occurs in two steps the second one making use of the heat content in the effluent from the oxygen reactor.

The hot slurry now contains the iodide in solution and is transferred into a settling tank where the potassium hydrogen carbonate is separated. The solid is forwarded to the calcinating furnace and further into the potassium carbonate reactor, R44. Here it is brought to react with mercury iodide vapor which is fed across from the ammonium iodide reactor, R43. The products from the carbonate reactor then enter the solution-slurry circuit, except for the oxygen which is vented.

The solution from the potassium hydrogen carbonate settling tank is cooled to ambient temperature and turned into a slurry of ammonium iodide. Some of the heat removed during this process is used to heat the slurry at a preceding stage in order to conserve heat. The ammonium iodide is separated from the dilute solution, dried, and passed on into the iodide reactor, R43. It reacts with mercury coming from the carbonate reactor, R44, and forms mercury iodide, ammonia, and the principal product, hydrogen. Mercury iodide is collected as a liquid to be used in the reactor R44, ammonia is scrubbed, and the hydrogen is collected.

The flow of reactants, the pattern of heat exchange and use of primary heat outlined here permits an estimate of the basic heat requirement for the cycle.

Primary heat is assumed to be used for the high-temperature reactions (4-3) and (4-4), for the calcination of the hydrogen carbonate, and to make up for losses not recoverable by heat exchangers. Direct losses of heat to the environment from the reactors and transfer lines because of imperfect insulation were not considered. A summary of the numbers used for the estimate is contained in Table 4. With reasonable assumptions about the efficiency of the heat exchange systems the total amount of heat that has to be supplied is 930 kilojoules per mol of hydrogen produced.

This result corresponds to an overall efficiency of heat converted into chemical potential energy (i.e. referred to the Gibbs energy of formation of water) of

$$\eta_{\text{ANL-4}} = 0.255$$

Though this number may seem small by comparison to the ideal value it is nevertheless respectable when compared to electrolysis, the only process by which hydrogen can be made without reliance on fossil fuels. Besides, it was arrived at as an overall efficiency based on a flow pattern reflecting the actual conditions under which the process can be conducted in a realistic manner.

In addition to the reasonable heat conversion efficiency the cycle ANL-4 has a number of attractive features. These include the clean chemistry of the important reactions, the low maximum temperature of 900 K, and the fact that the reactants permit efficient handling as liquids and slurries.

Against this stands the presence of mercury which may require special treatment of effluents, and the large volume of solvent that needs to be circulated. However, we believe this cycle is suitable to demonstrate the concept of thermochemical water splitting and offers the opportunity to acquire necessary information for reactor and heat exchanger design.

ACKNOWLEDGEMENT

We wish to thank Mr. Michael Grimm, Student Aide, for performing the chemical analyses.

Table 1. Entropy balance for the cycle ANI-4.

Operation	Entropy change ^a $\Delta S_{\text{reaction}}$ or $\int \frac{\Delta C_p}{T} dt$ J·K ⁻¹	Entropy of the system J·K ⁻¹
Heating of H ₂ O	$\int_{298.2}^{327.2} \frac{C_p}{T} dT = + 7.0$	+ 7.0
Reaction (4-1) at 327.2 K	$\Delta S = - 683.6$	- 676.6
Heating of 2KHCO ₃ + 2NH ₄ I	$\int_{327.2}^{430.1} \frac{\Sigma C_p}{T} dT = + 104.0$	- 572.6
Reaction (4-2) at 430.1 K	$\Delta S = + 300.0$	- 272.6
Heating of K ₂ CO ₃ + 2NH ₄ I	$\int_{430.1}^{538.4} \frac{\Sigma C_p}{T} dT = + 72.8$	- 199.8
Reaction (4-3) at 538.4 K	$\Delta S = + 413.4$	+ 213.6
Heating of K ₂ CO ₃ + HgI ₂	$\int_{538.4}^{810.8} \frac{\Sigma C_p}{T} dT = + 88.8$	+ 302.4
Reaction (4-4) at 810.8 K	$\Delta S = + 209.0$	+ 511.4
Cooling of 2KI + Hg + CO ₂ + 1/2 O ₂	$\int_{810.8}^{538.4} \frac{\Sigma C_p}{T} dT = - 84.6$	+ 426.8
Cooling of 2KI + 2NH ₃ + CO ₂ + H ₂ + 1/2 O ₂	$\int_{538.4}^{430.1} \frac{\Sigma C_p}{T} dT = - 64.2$	+ 362.6
Cooling of 2KI + 2NH ₃ + 2CO ₂ + H ₂ O + H ₂ + 1/2 O ₂	$\int_{430.1}^{373} \frac{\Sigma C_p}{T} dT = - 50.0$	+ 312.6
Condensation of H ₂ O at 373 K	$\Delta S = - 110.4$	+ 202.2
Cooling of 2KI + 2NH ₃ + 2CO ₂ + H ₂ O + H ₂ + 1/2 O ₂	$\int_{373}^{327.2} \frac{\Sigma C_p}{T} dT = - 51.2$	+ 151.0
Cooling of H ₂ + 1/2 O ₂	$\int_{327.2}^{298.2} \frac{\Sigma C_p}{T} dT = - 7.8$	+ 143.2
Reaction H ₂ + 1/2 O ₂ = H ₂ O at 298.2 K	$\Delta S = - 143.2$	0.0

^aThe calculated entropy changes were individually adjusted by no more than 1.3% to obtain overall balance for the cycle.

Table 2. Solution behavior of mixtures of KI and NH_4HCO_3 in various solvents
(Sampling temperature: 298.2 K)

Solvent	Gas atmosphere	Cation ratio NH_4^+/K^+	Anion ratio $\text{I}^-/\text{HCO}_3^-$	Concentration of solute mol/1000g solvent
H_2O	air, 1 atm	1.1	3.5	7.6
H_2O	air, 1 atm	1.1	1.8	8.5
Ethanol- H_2O 3:1	NH_3+CO_2 , 3.7 atm	1.7	11.7	1.8
Ethanol- H_2O 7:1	CO_2 , 3.9 atm	0.7	25.0	1.0
Isopropanol- H_2O 3:1	CO_2 , 4.9 atm	2.1	11.8	1.8
Isopropanol- H_2O 7:1	CO_2 , 4.4 atm	3.4	13.9	0.7

Table 3. Equilibrium constants for the reaction $2\text{NH}_4\text{I}(\text{g}) + \text{Hg}(\text{g}) \rightleftharpoons 2\text{NH}_3 + \text{HgI}_2(\text{g}) + \text{H}_2$

Temperature K	Initial charge mmol		Amount H_2 recovered mmol	Kp experimental	Kp calculated
	NH_4I	Hg			
731	3.26	4.49	1.59	1011	936
783	2.90	5.28	1.39	216	225

Table 4. Heat tally for cycle ANL-4.

	Heat required kilojoules	Heat supplied from primary source kilojoules	Heat recovered through heat exchanger systems kilojoules
Reaction (4-1)	475	0	475
Drying & heating of KHCO_3	105	105	0
Reaction (4-2)	135	135	0
Vaporization of Hg	70	2	68
Drying of NH_4I	99	99	0
Heating of NH_4I	123	123	0
Reaction (4-3)	235	235	0
Vaporization of HgI_2	104	34	70
Heating of K_2CO_3	84	84	0
Reaction (4-4)	175	175	0
Total heat	1543	930	613
Efficiency of conversion: $\eta_{\text{ANL-4}} = \frac{237}{930} = 0.255$			

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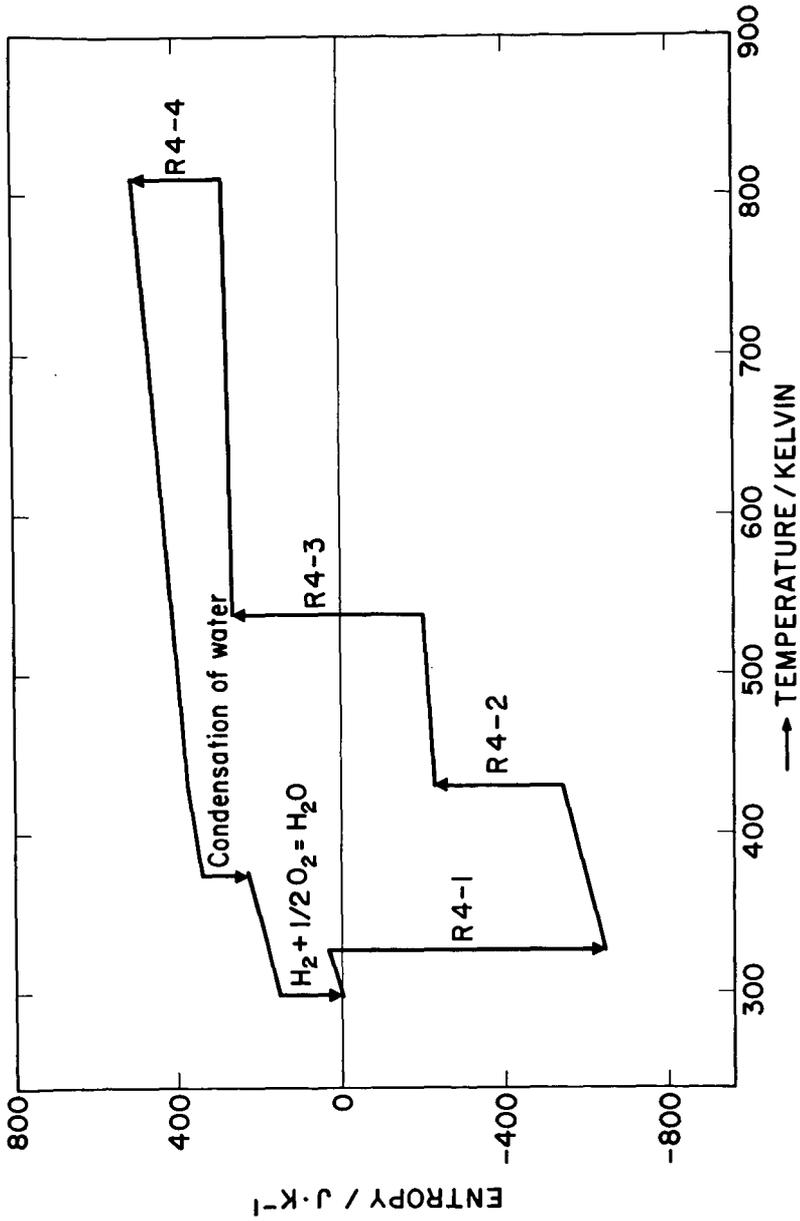


Figure 1. Entropy-temperature diagram for thermochemical water splitting cycle ANL-4. The area enclosed by the diagram equals the Gibbs energy for the decomposition of water into the elements at the standard states.

