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Preliminary Flow Sheet and Process Design for ZnSe Thermochemical Cycle

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June 21, 1976

Prepared for U.S. Energy Research & Development Administration under contract No. W-7405-Eng-48.

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ABSTRACT

A preliminary design of the ZnSe cycle for thermochemical hydrogen production has been prepared for use in deriving economic costs for hydrogen production. The process flowsheet identifies key equipment items as well as major streams. Flow and heat loads have been estimated based on one mole of hydrogen output.

The thermal efficiency of this cycle depends on two factors: (1) the ability to perform the dissolution of $ZnSO_4$ and the hydrolysis of ZnSe with a minimum amount of aqueous HCl, and (2) the ability to match the process heat requirements with available heat from the exothermic steps in the cycle. Estimates of the cycle's thermal efficiency range from 34-57% depending upon the process heat utilization.

Work performed under the auspices of the U.S. Energy Research & Development Administration under contract No. W-7405-Eng-48.

Introduction:

Water decomposition processes for hydrogen production appear to be an attractive means of obtaining a synthetic fuel from a high temperature heat source. A thermochemical process consists of a closed set of chemical reactions, the net sum of which amounts to water decomposing into its elements, hydrogen and oxygen, with all other intermediate chemical species being recovered and recirculated. These processes promise an efficiency, defined as the ratio of hydrogen output to thermal input, higher than that for thermal energy to work conversion followed by water electroysis.

Key criteria in the selection of a thermochemical process are the following:

- Favorable thermodynamics
- High (40-50%) thermal efficiency
- Fast reaction rates
- High conversion, thus avoiding massive recycling of unreacted species.
- Inexpensive chemical intermediates.

A thermochemical process based on the chemistry of zinc and selenium developed at the Lawrence Livermore Laboratory (1) appears to be of promise for further development based on these criteria with the possible exception of the final one. Selenium, though costly, can be recycled at high recovery rates adding to the overall cost only as a portion of the plant inventory.

This report describes a preliminary engineering evaluation of the Zn-Se cycle. A flowsheet of the process has been prepared including mass and energy balances. Major items of equipment have been designed from a conceptual viewpoint to provide guidance for a more complete plant design that will include plant economics and arrive at a final figure for hydrogen cost.

Process Description:

The ZnSe thermochemical cycle for hydrogen production has been studied experimentally in the laboratory and results are available in the literature (1,2,3). The ZnSe cycle was concluded to be a scientifically feasible thermochemical cycle on the basis of these experimental results. The basic reactions and the temperatures at which they occur are shown in Table 1.

A key step (Rx.1) is the reaction of solid ZnO with liquid Se and gaseous SO_2 to produce a mixture of $ZnSO_4$ and ZnSe. The second major step (Rx.3) is the hydrolysis of ZnSe to yield H_2Se. The remaining reactions in the cycle are those used to generate hydrogen and oxygen and to regenerate the starting materials.

Key issues to be determined from a chemical engineering viewpoint include: (1) consideration of the major endothermic and exothermic heat loads in the cycle to allow for efficient heat-matching, (2) the thermal load required to evaporate the additional water introduced with the aqeuous HCl streams and (3) the determination of the overall cycle thermal efficiency.

Important too are the methods used to separate the various chemical species, i.e., H_2 from H_2Se and SO_2 from O_2, as well as ensuring that little or no Se is lost. The detailed work following includes a preliminary flowsheet for the process described in Table I together with completed material and energy balances. Process conditions including estimates of the residence time, temperature, pressure and degree of conversion for each reaction are given for the major process steps.

Flow Sheet and Process Design:

A preliminary flow sheet for the ZnSe thermochemical cycle has been developed based on the most recent laboratory results(see Figure 1). Key items (reactors and separators) are given in Table 2, and the contents of individual streams have been identified in the flow sheet. Material and energy balances have been completed for individual components as well as the overall stream on a molar basis. The mole quantities as well as the temperature and pressure for each stream based on the production of one mole of hydrogen are given in Table 3. An estimate for the residence time and the degree of conversion is given in Table 4. The exothermic and endothermic heats of reaction were estimated from tables of thermodynamic data (4,5) and are tabulated in Table 5 along with the process heat exchanger loads.

Battery A

The principal function of Battery A is to carry out the reaction (1): $2\ ZnO(s) + Se(l) + SO_2(g) = ZnSe(s) + ZnSO_4(s)$. Battery A consists of a high temperature reactor equipped with heat exchangers connected to a separator to remove SO_2 from the reaction products.

The ZnSe synthesis reaction is carried out with a 50 mole % excess of selenium and a 5 atmosphere overpressure of SO_2. It is estimated to go to completion in roughly 10 minutes at 800K. The reaction being -161 kj exothermic per mole of Se reacted, liberates substantial heat for other process use. Since the reactants ZnO(s) and Se(l) must be introduced and products ZnSe(s), Se(l) and $ZnSO_4(s)$ be withdrawn from the pressurized reactor, the reactor design will be fairly complex. The product stream is cooled to room temperature before entering separator S-1 where the solids are disengaged from the gaseous SO_2. This $SO_2(g)$ separation must be complete as trace SO_2 will cause an undesirable side reaction in subsequent steps producing sulfur. The SO_2 gas is recycled back to (R-1). The solid products are sent to Battery B.

Battery B

The function of Battery B is to separate one of the reaction products, $ZnSO_4$, since the pressure of $ZnSO_4$ interferes with the hydrolysis of ZnSe and produces undesirable by-products. Battery B consists of a dissolver, an evaporator, and a dryer. When the solid products from Battery A are introduced into a 6 N HCl solution (20 wt % HCl solution) in the dissolver, $ZnSO_4$ is preferentially leached. A minimum of acid is used to completely dissolve the $ZnSO_4$ (~4 to 5 H_2O per $ZnSO_4$) since subsequent recovery of $ZnSO_4$ for recycle will require boiling of the HCl/H_2O solutions. The undissolved ZnSe and Se are separated from the solution and sent to Battery C. The concentrated solution of $ZnSO_4$ in HCl/H_2O is piped to the evaporator S-2 where the HCl/H_2O azeotropic mixture is boiled off, condensed and recycled back to the dissolver (R-2). That $ZnSO_4 \cdot H_2O$ will crystallize out of the supersaturated solution has been verified by a laboratory experiment using X-ray crystallography to identify the precipitate. The amount of HCl/H_2O azeotrope boiled off corresponds to about 3 moles of H_2O equivalent per mole of $ZnSO_4 \cdot H_2O$ recovered. The $ZnSO_4 \cdot H_2O$ solid is now transferred to a dryer in which the water of hydration is removed, the water being recycled to dissolver R-2 while the anhydrous $ZnSO_4$ from S-8 is added to the

the $ZnSO_4$ stream from the Battery D and the combined stream is routed to the $ZnSO_4$ decomposer R-5 of Battery E.

Battery C

One of the most important process steps, the hydrolysis of ZnSe, is performed in Battery C. The reaction is: $ZnSe(s) + 2HCl(aq) = ZnCl_2(aq) + H_2Se(g)$. Battery C consists of a hydrolyzer, a concentrator, and a crystallizer. As HCl reacts with the ZnSe(s), one of the products, gaseous H_2Se, which is virtually insoluble in the aqueous phase, separates. The $H_2Se(g)$ is scrubbed with the feed water to remove trace HCl(g) and piped to Battery G. The HCl consumed in the hydrolysis reaction is introduced as gaseous HCl from Battery E in two separate locations: (1) to the R-3 hydrolyzer to maintain the desired approximately 6 N HCl (20 wt %) concentration in the exit stream and, (2) to crystallizer S-4 to enhance crystallization relying on the common ion effect. The unreacted solid Se is separated from the $ZnCl_2$-HCl solution for recycle to R-1 of Battery A. The water/$ZnCl_2$ mole ratio in the exit stream from the hydrolyzer to the concentrator is maintained at about 3.5 to 1 to minimize the amount of evaporation that will be needed in the concentrator to produce a saturated solution at 375K. The boil-off is about 2.5 moles of H_2O equivalent per mole of $ZnCl_2$ crystallized. The saturated solution (~40 mole $ZnCl_2$/liter H_2O) is drawn from concentrator (S-2) and transferred to crystallizer (S-4), cooled to room temperature and saturated with HCl(g), crystallizing out a $ZnCl_2 \cdot 1/2\ HCl \cdot H_2O$ adduct. The crystals are separated and transferred to R-4 in Battery D. The remaining saturated solution containing about 18 mole $ZnCl_2$/liter H_2O is reheated and recycled to hydrolyzer R-3.

Battery D

The major function of this battery is to convert the $ZnCl_2 \cdot 1/2\ HCl \cdot H_2O$ adduct from the Battery C to $ZnSO_4$ and gaseous HCl. When $ZnCl_2$ adduct is contacted in the reactor, R-4, with a concentrated aqueous solution of sulfuric acid, anhydrous $ZnSO_4$ is precipitated. This occurs when the sulfuric acid concentration is between 85 and 95 wt % as seen from the $ZnSO_4$-H_2SO_4-H_2O solubility diagram, Figure 2. HCl is virtually insoluble in the concentrated H_2SO_4 and is taken off the top of R-4 as anhydrous HCl gas and recycled to Batteries B and C. $ZnSO_4$ is withdrawn, freed from the supernatant H_2SO_4 solution and routed with the $ZnSO_4$ from S-8 to the decomposer in Battery E.

The sulfuric acid solution now containing one mole of water, introduced into R-4 as part of the $ZnCl_2 \cdot 1/2\ HCl \cdot H_2O$ adduct from Battery C, is circulated through the absorber S-5 (probably a packed column) in which the consumed H_2SO_4 is regenerated. When SO_3 in the gaseous stream from Battery E is contacted with the H_2SO_4 acid solution from R-4 it reacts to form $H_2S_2O_7$ which subsequently reacts with H_2O to form 2 H_2SO_4. The absorber serves a dual function in that it removes SO_3 from the SO_3-SO_2-O_2 stream from Battery E prior to SO_2-O_2 separation in Battery F.

Battery E

In Battery E we perform the decomposition of $ZnSO_4$. Two moles of anhydrous $ZnSO_4$ per mole of hydrogen output are decomposed at ~1150-1200 K. The decomposition products are ZnO, SO_3, SO_2, and O_2. The composition of the gaseous product is dictated by the equilibrium

$$ZnSO_4 = ZnO + a\ SO_2 + (1-a)\ SO_3 + a/2\ O_2$$

as shown in Figure 3 and is determined by the decomposition temperature. Since the process requirements are for the SO_3/SO_2 ratio to be unity, the gas composition must be adusted. This is accomplished with a catalytic converter placed at the appropriate spot in the cool down heat exchanger. The gas stream adjusted in composition is directed to absorber S-5 of Battery D. The ZnO is returned to reactor R-1 of Battery A to restart the cycle.

The decomposition reaction is +586 kj/mole of H_2 endothermic, thus the major process heat input occurs in R-5. The gaseous decomposition products will be recirculated through the heat exchanger H-50 to absorb and transport the heat necessary to decompose the $ZnSO_4$. As the sensible heat of the gas mixture is used for transporting the enormous amount of "heat of reaction" required, a large gas circulation rate must be maintained. To operate at one atmosphere total gas pressure a decomposition temperature greater than 1160K must be attained. Thus, potential design problems mainly in the heat transfer area are foreseen for Battery E. Additionally the power requirements for circulation would tend to be much larger than that used to circulate lower temperature gases. An alternate method of providing the heat to decompose $ZnSO_4$ may have to be devised to overcome these difficulties.

Rate data for the thermal decomposition of metal sulfates is available in the literature (7). Significant changes in the rate are observed on addition of 1-5 wt % of a metal oxide (e.g., Fe_2O_3,Cr_2O_3) catalyst. The catalytic decomposition of $ZnSO_4$,though not considered in the present flowsheet, may offer the advantage of a shorter residence time and lower cost in reactor R-5. Calculations (8) based on the earlier Russian work show 95% completion of the decomposition reaction at 1200K in 14 minutes. Complete details are provided in Tables 6A and 6B.

Battery F

This battery provides for separation of SO_2 and O_2 using a compression and cryogenic cooling process. The SO_2 and O_2 mixture is compressed and the SO_2 is recovered by condensation with cooling water and finally with liquid O_2. The refrigeration is accomplished by expansion of the oxygen stream prior to venting. The SO_2 stream is returned to reactor R-1 in Battery A completing its cycle. It is possible to compute the theoretical separation work and estimate the required heat equivalent:

$$W_{theor.} = -RT \sum (n_k \ln x_k)$$

$$= +2.38 \text{ kj/mole } H_2$$

$$Q_{separ.} = 14.3 \text{ kj/mole } H_2 \text{ (Q/W taken as 6).}$$

The design of this part of the ZnSe cycle would resemble that of the Westinghouse sulfur cycle (9) which involves the same separation.

Battery G

Battery G's main function is to decompose H_2Se into its constituents, H_2 and Se(l). The decomposition reaction is exothermic and proceeds rapidly at temperatures above ~550K. Decomposition behavior from the literature (9) is shown in Figure 4. At 550K, decomposition is 80% complete at equilibrium, thus necessitating recycle of the undecomposed H_2Se to the inlet of reactor R-6. The H_2Se - H_2 mixture is separated in S-7. This unit will probably resemble Battery F in which SO_2 and O_2 are separated from one another. Separation will be accomplished by compression of the gas, its subsequent expansion and cooling. The product hydrogen stream, after scrubing free of Se and H_2Se (for toxicity reasons) is then compressed to 3 MPa(30atm) for pipeline or chemical feedstock use. The liquid Se is recycled to Battery A and fed into reactor R-1 to complete the Se part of the cycle. This Se may be used to coat the ZnO particles from Battery E, reactor R-5, thus forming the intimate mixture needed for the reaction of these two chemical species with SO_2 in reactor R-1.

Separation work or its heat equivalent will have to be supplied to S-7 to effect the H_2, H_2Se separation. The theoretical work and equivalent heat of separation are estimated as:

$$W_{theor.} = -(1.986)(4.184(300)\left[\ln(.8) + .25\ \ln(.2)\right]$$

$$= +1.56\ \text{kj/mole}\ H_2$$

$$Q_{separ.} = 9.4\ \text{kj/mole}\ H_2\ (Q/W\ \text{taken as}\ 6).$$

Plant Thermal Efficiency:

The major endothermic and exothermic heat loads of the ZnSe cycle are shown in Table 5. It is very important from an efficiency standpoint to match the process heat requirements with available heat from the exothermic steps in the cycle.

Two major efficiency determining heat loads become apparent when the data in Table 5 are studied. First, the largest endothermic heat load is supplied in exchanger H-50. (The heat exchanger numbering scheme uses the number of the reactor for the first numeral, so that, for example, exchanger H-50 corresponds to reactor R-5) This heat is used for the decomposition of 2 moles of $ZnSO_4$ and amounts to 586 kj/mole H_2 at the temperature of the decomposition step. Second, a major portion of the remainder of the heat requirement is due to the evaporation of the HCl-H_2O azeotropes in Batteries B and C. These heat loads involve exchangers H-21 and H-33, amounting to a load of 286 kj/mole H_2. To offer a comparison, the higher heating value of H_2 is -286 kj/mole. Although it is not possible to reduce the total endothermic requirement for $ZnSO_4$ decomposition, by judicious management of the remainder of the streams, it should be possible to minimize any additional cycle heat requirements.

It is also extremely important, especially in the ZnSe cycle, to minimize the amount of HCl-H_2O azeotrope that has to be evaporated. Little of the latent heat of evaporation can be recovered for reuse due to the low temperature. What this means, in effect, is that we need to develop improved chemical methods to lower the amount of water added in Battery B and C for the separation of $ZnSO_4$ from ZnSe and the hydrolysis of ZnSe.

Referring again to Table 5, a preliminary estimate of the overall efficiency (η) to be expected from this cycle is obtained from the net difference in the endothermic and exothermic heat loads in the Table and the estimate for heat equivalent to the work of separation (Battery F, SO_2/O_2; Battery G, H_2/H_2Se) developed earlier. Care must be exercised in the use of these latter results as the actual energy requirement for gas separation may exceed these estimates. Thus, 1191 kj-694kj = 497 kj/mole is the net endothermic heat requirement and using 286 kj/mole as the negative of the higher heating value of hydrogen, we have:

$$\eta_1 = \frac{286}{497} = 57\%$$

Practically though, if we deduct the H-20 exothermic heat load (heat of solution of $ZnSO_4$ anhydrous) as being at a temperature too low for use (see Table 4), we obtain: 1191kj-548kj = 643kj/mole as the net endothermic heat to be supplied. Then, for the thermal efficiency of the cycle, we have:

$$\eta_2 = \frac{286}{643} = 44\%$$

Alternatively, if we assume that the H-30 heat load is unusable, we obtain, 1191kj-36kj = 830kj/mole, as the net endothermic heat, and:

$$\eta_3 = \frac{286}{830} = 34\%.$$

The values above, 57% (η_1) and 34% (η_3) appear to represent the range of efficiency achievable with the ZnSe cycle.

The overall cycle efficiency is highly dependent on recuperative heat exchange; as much as possible of the exothermic heat in the process should be put to use. It is worth considering doing the $ZnSO_4$ dissolution at a high enough temperature to avoid losing 146kj/mole of energy, and to perform the ZnSe hydrolysis at a temperature (>373K) high enough to recover an additional 156kj/mole. These two heat loads amounting to 302kj/mole will have a major impact on the overall thermal efficiency. This observation emphasizes the need for energy conservation in the process design of thermochemical cycles for water decomposition.

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Table 1

The ZnSe Thermochemical Cycle *

	Reaction	T(K)
1.	$2\ ZnO + Se(l) + SO_2(g) = ZnSe + ZnSO_4$	800
2.	$ZnSe + ZnSO_4 \overset{(aq\ HCl)}{=} ZnSO_4(aq) + ZnSe$	400
3a.	$ZnSe + 2\ HCl(aq) = ZnCl_2(aq) + H_2Se(g)$	400
3b.	$ZnCl_2(aq) + 1/2\ HCl(aq) + H_2O(\ell) = ZnCl_2 \cdot 1/2\ HCl \cdot H_2O$	300
4a.	$H_2SO_4(aq) + H_2O(l) + SO_3(g) = 2\ H_2SO_4(aq)$	400
4b.	$H_2SO_4(aq) + ZnCl_2 \cdot 1/2\ HCl \cdot H_2O = ZnSO_4 + 5/2\ HCl(g) + H_2O(\ell)$	400
5.	$2\ ZnSO_4 = 2\ ZnO + SO_3(g) + SO_2(g) + 0.5\ O_2(g)$	1160
6.	$H_2Se(g) = H_2(g) + Se(l)$	550

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* Reaction numbers are listed to correspond to the reactor numbers given in Table 2, i.e., reaction 1 above would be carried out in reactor R-1. The chemical substances are solids unless designated otherwise.

Table 2

Major Equipment List for the ZnSe Cycle

Item No.	Description
R-1	Primary Reactor (ZnO, Se, SO_2)
R-2	$ZnSO_4$ Dissolver/Separator
R-3	ZnSe Hydrolyzer (H_2Se Generator)
R-4	HCl Regenerator/$ZnSO_4$ Crystallizer
R-5	$ZnSO_4$ Decomposer
R-6	H_2Se Decomposer
S-1	Solid/Gas Disengager
S-2	Evaporator/Crystallizer
S-3	Evaporator/Concentrator
S-4	Crystallizer
S-5	Stripper/Absorber (H_2SO_4 Regenerator)
S-6	Separator (Product - O_2)
S-7	Separator (Product - H_2)
S-8	Dehydrator

Table 3

Material Balance for the ZnSe Cycle
(mole per mole of hydrogen production)

Stream No.		1	2	3	4	5	6	7	8	9	10
Temp(K)		800	800	800	800	400	400	400	400	400	400
Press(Atm)		5	Solid	1	5	1	Solids	1	1	1	-
Component	Mol.Wt.										
H_2O	18							1	1.35	2.5	
H_2	2										
O_2	32										
SO_3	80										
SO_2	64	1			T*	T					
H_2SO_4	98										
ZnO	81.4		2		T		T				
$ZnSO_4$	161.4				1		1				
$ZnSO_4 \cdot H_2O$	179.4										
ZnSe	144.4				1		1				
Se	79			1.5	0.5		0.5				
H_2Se	81										
HCl	36.5								0.15	0.27	T (g)
$ZnCl_2$	136.4								1.1		

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* T - trace

Table 3 (continued)

Stream No.	11	12	13	14	15	16	17	18	19	20
Temp(K)	400	400	400	400	400	400	400	400	400	400
Press(Atm)	Solid	Solid	1	Solid	1	1	2	2	2	1
H_2O			6	1		1				3.85
H_2										
O_2										
SO_3										
SO_2										
H_2SO_4					1(ℓ)	1(s)				
ZnO		T								
$ZnSO_4$		T								
$ZnSO_4 \cdot H_2O$	1(s)		1(s)							
ZnSe	1	1								
Se	0.5	0.5								
H_2Se										
HCl	1(s)	T	1(s)	0.5			2.5(g)	1.5(g)	1.0(g)	0.42
$ZnCl_2$				1						1.1

Table 3 (continued)

Stream No.	21	22	23	24	25	26	27	28	29	30
Temp(K)	400	300	400	300	550	550	550	550	300	400
Press(Atm)	5	1	1	1	5	5	5	1	30	1
H_2O		0.35	5	1						
H_2							1		1	
O_2										
SO_3										
SO_2										
H_2SO_4										
ZnO										T
$ZnSO_4$										
$ZnSO_4 \cdot H_2O$										
ZnSe										
Se								1		0.5
H_2Se	1.0				0.25	1.25	0.25			
HCl		0.11	0.54							
$ZnCl_2$		0.1								

Table 3 (continued)

Stream No.	31	32	33	34	35	36	37	38	39	40
Temp(K)	400 1000	400	300 800	300 1	1000 400	400 1000	400 1000			
Press(Atm)	Solid	1	5	1	1	(Solid)	Solid			
H_2O										
H_2										
O_2		0.5		0.5	0.5					
SO_3					1					
SO_2		1	1		1					
H_2SO_4										
ZnO										
$ZnSO_4$	1					1	2			
$ZnSO_4 \cdot H_2O$										
ZnSe										
Se										
H_2Se										
HCl										
$ZnCl_2$										

Table 4

Reaction Residence Times Required for Various Reactors and Separators

	Residence Time (h)	% Conversion or Separation	Pressure (atm)	Temp.(K)
R-1	0.1-0.3	100%	5 atm SO_2	800
R-2	<0.1	100% $ZnSO_4$ dis.	~2 atm HCl	350
R-3	0.05-0.15	100% ZnSe	5 atm H_2Se	400
R-4	0.25	100% HCl	2 atm HCl	400
R-5	0.2-0.4	100%	~1.0 atm	1200
R-6	0.01	80%	5 atm H_2Se/H_2	550
S-1	0.1	100%	<0.01 atm SO_2	350
S-2	0.15	--	1 atm HCl/H_2O	382
S-3	0.10	--	1 atm HCl/H_2O	382
S-4	0.25	90%	--	300
S-5	0.05	100% SO_3 abs.	0.6 atm SO_2+O_2	400
S-6	0.1	100%	--	<300
S-7	0.1	100%	--	<300
S-8	0.1	100%	--	500

Table 5

Heat Exchanger Loads for the ZnSe Cycle

Heat Exchanger No.	Streams or Units	Material	Moles	Heat Cap. C_p(cal/mole-K)	Temp(K) In	Temp(K) Out	Enthalpy Load (kJ/mole H_2)
H-10	R-1	Reaction 1	--	--	800	800	-160.6
H-11	3	Se	1.5	7.0	550	800	+11.0
H-12	4	Reaction Prod's	2.5	49.8	800	400	-83.4
H-13	33	SO_2	1.0	12.0	300	800	+25.1
H-20	R-2	$ZnSO_4$ in Soln.	--	--	300	300	-146
H-21	S-2	$H_2O \cdot HCl \cdot ZnSO_4$	3.0(H_2O)	--	382	382	+156
H-22	S-8	$ZnSO_4 \cdot H_2O$	1.0	--	500	500	+80
H-30	R-3	H_2Se generation	1.0	--	382	382	-156
H-31	21	H_2Se	1.0	10.0	400	550	+6.3
H-32	30	Se	0.5	7.0 & ΔH of Fusion	400	550	+7.5
H-33	S-3	$HCl \cdot H_2O \cdot ZnCl_2$	2.5(H_2O)	--	382	382	+130
H-34	22	$HCl \cdot H_2O \cdot ZnCl_2$	--	18	300	400	+2.5
H-35	S-4	$HCl \cdot H_2O \cdot ZnCl_2$	--	18	382	300	-8.0
H-50	R-5	$ZnSO_4$ Decomp	2.0	--	1100	1100	+586.
H-51	2	ZnO	2.0	12.5	1150	800	-36.6
H-52	37	$ZnSO_4$	2.0	33.7	450	1000	+155
H-53	35	$SO_3 \cdot SO_2 \cdot 1/2\ O_2$	2.5	13.5	1000	400	-84.6
H-60	R-6	H_2Se Decom	1.0	--	550	550	-18.7

Table 6A

Summary of Rate Constant Data for $ZnSO_4$ Decomposition from Pechkovskii et al.(7), as Analysed by Krikorian (8). For Method of Analysis see Below.

	$ZnSO_4$		$ZnSO_4$+ 5% Cr_2O_3		$ZnSO_4$+ 5% CuO		$ZnSO_4$+ 5% Fe_2O_3	
T,K	k_1	k_2	k_1	k_2	k_1	k_2	k_1	k_2
1050	0.00125	0.00013	0.0026	0.00038	0.0080	0.00090	0.0106	0.0026
1100	0.0058	0.00103	0.0114	0.0027	0.022	0.0044	0.025	0.0070
1150	0.023	0.0070	0.044	0.0162	0.060	0.020	0.054	0.0177
1200	0.084	0.041	0.154	0.083	0.145	0.080	0.109	0.041
1250	0.27	0.20	0.48	0.36	0.33	0.28	0.21	0.089

Method of Data Analysis: Decomposition Rate Expression as Given by Pechkovskii is:

$$(1 - \alpha)^{1/3} = 1 - k\tau,$$

where α = fraction reacted

τ = time in minutes

k = rate constant

Assume k, applies from $\tau = 0$ to $\tau = \tau_1$, and from $\alpha = 0$ to $\alpha = 0.30$,

Also k_2 applies from $\alpha = 0.30$ to $\alpha = 1.00$.

Then:

$$\tau_1 = \frac{1 - (1-\alpha_1)^{1/3}}{k_1} = \frac{0.1121}{k_1} = \text{time for 30\% completion.}$$

$$\tau_2 = \tau_1 + \frac{\Delta(1-\alpha)^{1/3}}{k_2} = \tau_1 + \frac{(1-\alpha_2)^{1/3} - 0.8879}{k_2} =$$

time for > 30% completion.

Table 6B

Summary of Time (T_1 or T_2) Required for Various Degrees of Completion of $ZnSO_4$ Decomposition Reaction

			T_2 for Various % Completion			
Material	T,K	T_1(30% Completion)	90%	95%	98%	100%
$ZnSO_4$	1050	89.7 min.	3349 min.	4086 min.	4832 min.	6920 min.
	1100	19.3	431	524	618	881
	1150	4.9	65.4	79.1	93.0	131.7
	1200	1.3	11.6	14.0	16.3	23.0
	1250	0.4	2.5	3.0	3.5	4.8
$ZnSO_4$ + 5%Cr_2O_3	1050	43.1	1158	1410	1665	2380
	1100	9.8	166.7	202	238	339
	1150	2.5	28.7	34.6	40.6	57.3
	1200	0.7	5.8	7.0	8.1	11.4
	1250	0.2	1.4	1.6	1.9	2.7
$ZnSO_4$ + 5% CuO	1050	14.0	485	591	699	1001
	1100	5.1	101.4	123.2	145.2	207
	1150	1.9	23.1	27.9	32.7	46.3
	1200	0.8	6.1	7.3	8.5	11.9
	1250	0.3	1.8	2.2	2.5	3.5
$ZnSO_4$ + 5%Fe_2O_3	1050	10.6	173.6	210	248	352
	1100	4.5	65.0	78.7	92.6	131.3
	1150	2.1	26.0	31.5	36.9	52.3
	1200	1.0	11.3	13.7	16.0	22.7
	1250	0.5	5.3	6.3	7.4	10.5

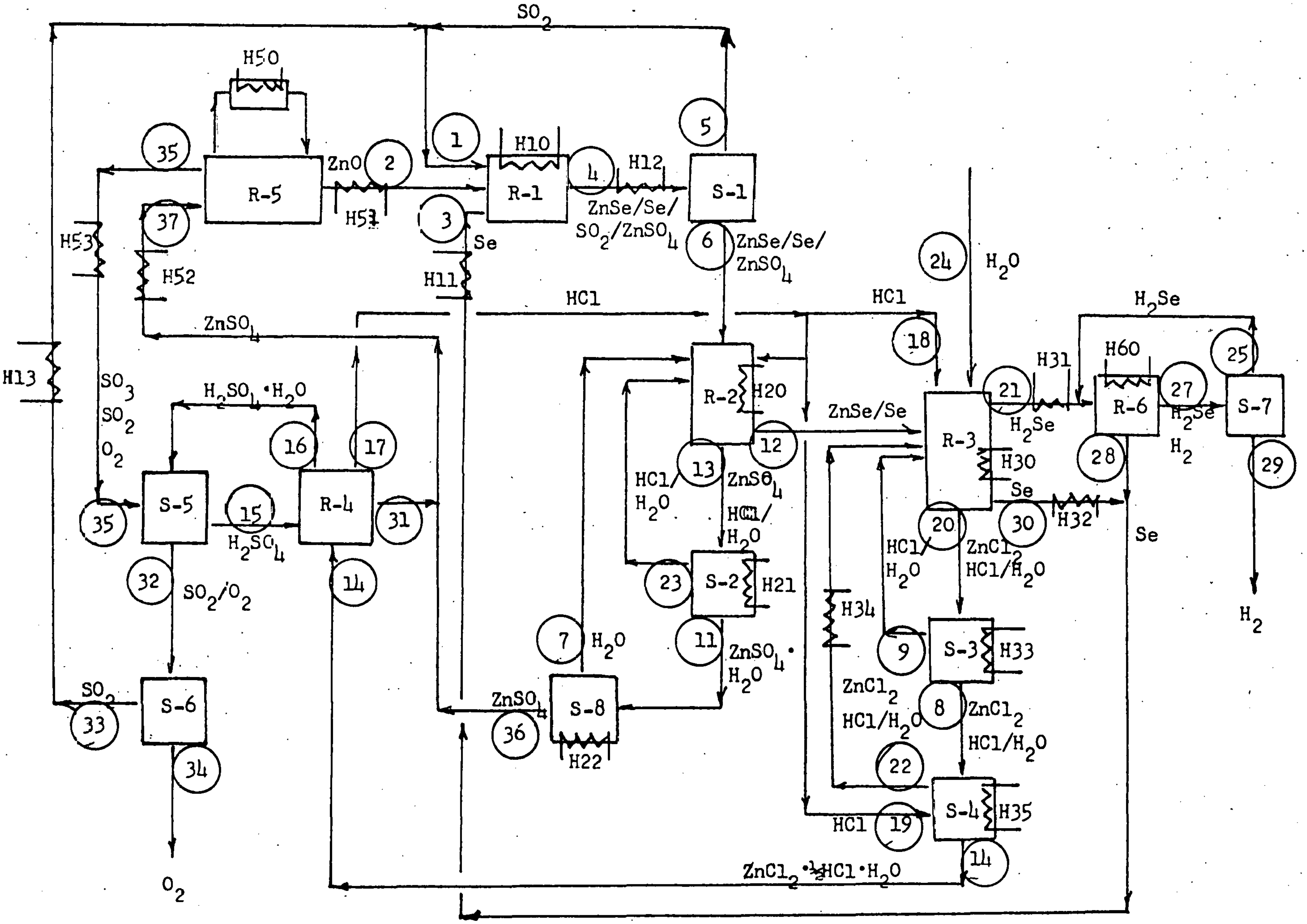


Figure 1. Flowsheet of the ZnSe Cycle for Water Decomposition

Figure 2

Solubility of $ZnSO_4$-H_2SO_4-H_2O at 25°C

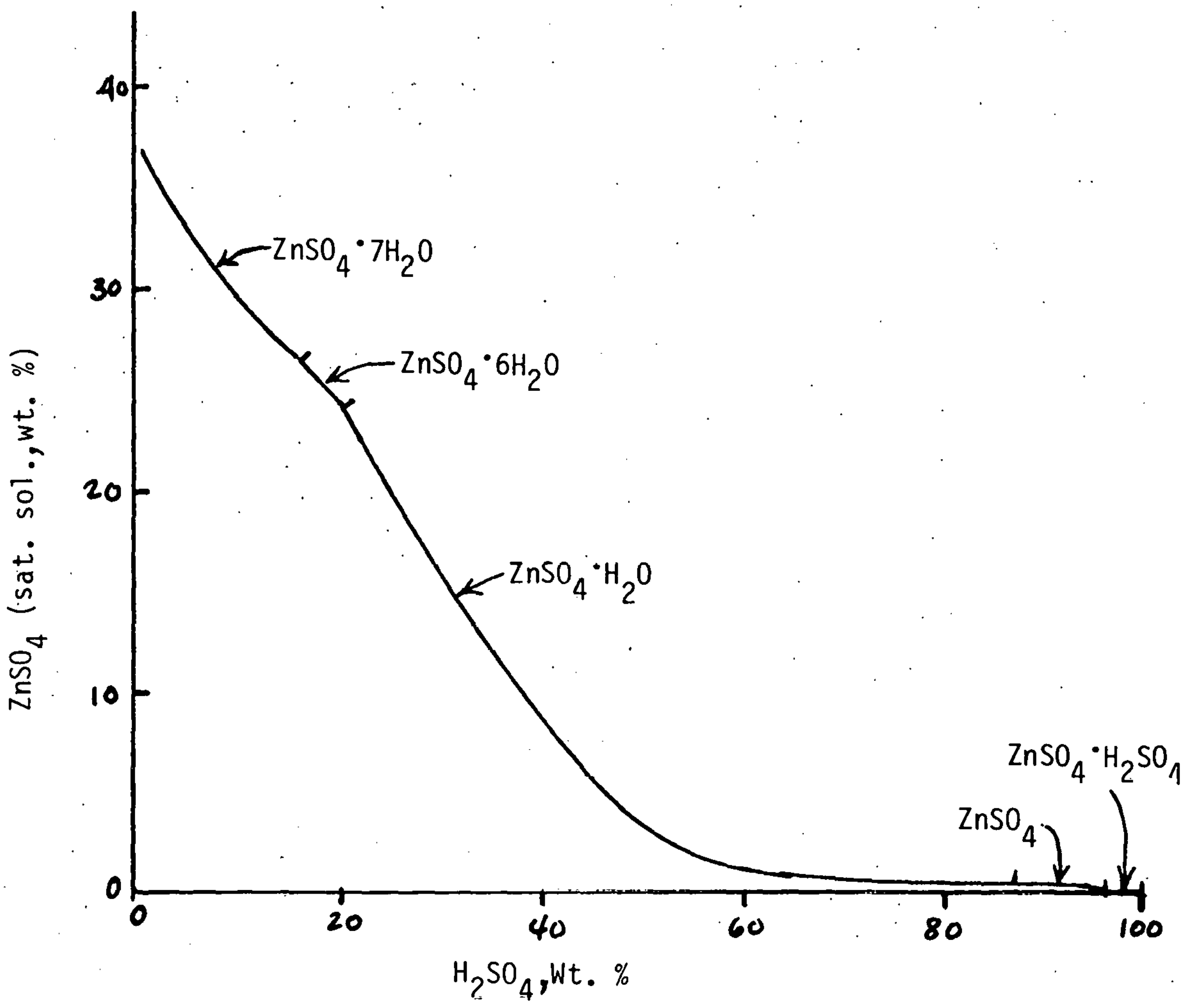
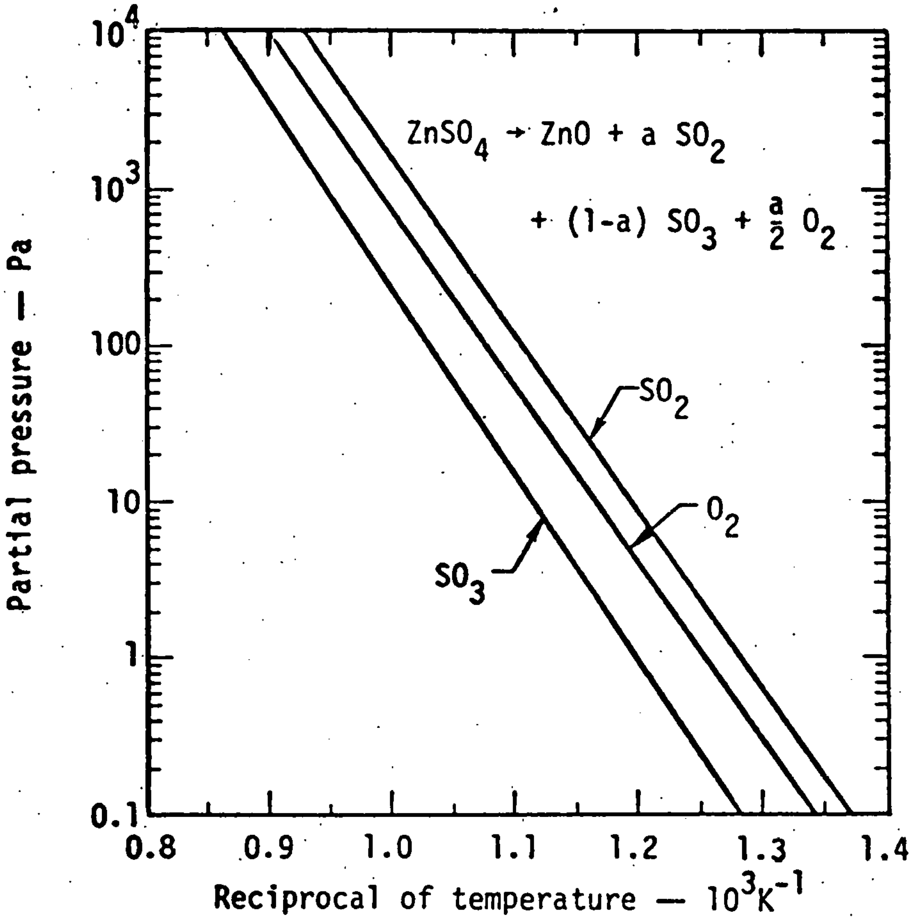
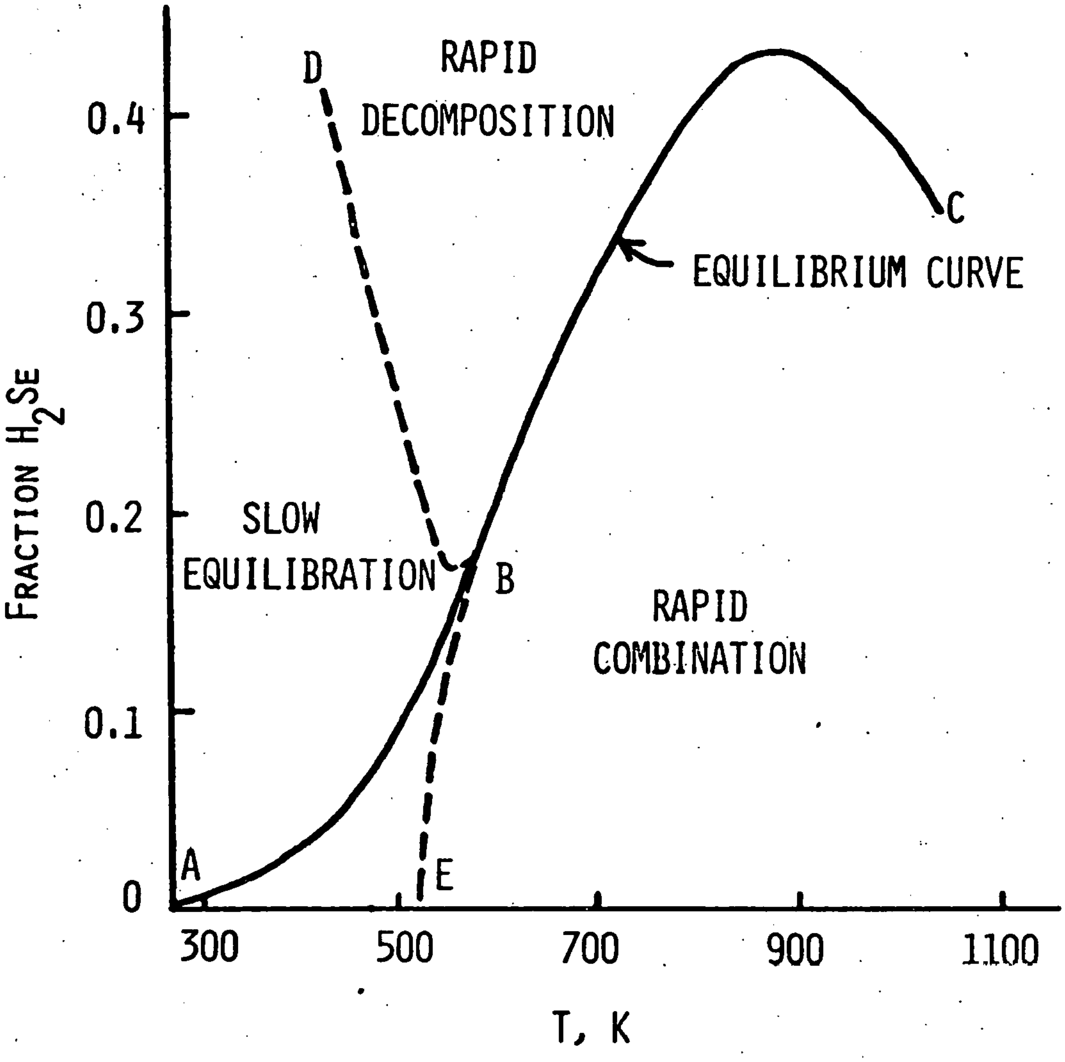


Figure 3



Equilibrium partial pressures of SO_2, SO_3, and O_2 over $ZnSO_4$ as a function of temperature. (10^5 Pa = 1 atm)

Figure 4



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