NASA TECHNICAL MEMORANDUM NASA TM-77787

(NASA-TM-77787) STUDY OF THE LIQUID VAPOR
EQUILIBRIUM IN THE BROMINE-HYDROBROMIC
ACID-WATER SYSTEM (National Aeronautics and
Space Administration) 17 p HC A02/MF A01
CSCL 07D G3/25

N85-15836

Unclas
13473

STUDY OF THE LIQUID-VAPOR EQUILIBRIUM IN THE BROMINE-HYDROBROMIC ACID-WATER SYSTEM

R. Benizri, P. Lessart, P. Courvoisier

Translation of "Etude de l'equilibre de phases liquides-gaz dans le systeme brome-acide bromhydrique-eau". In: Communication of the European Communities". Report EUR 6783, 1980, Hydrogen Energy Vector, pp 101-116.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON D.C. 20546 DECEMBER 1984

STANDARD TITLE PAGE

1. Report No. NASA TM-77787

2. Government Accession No.

3. Recipient's Catalog No.

4. Title and Subtitle STUDY OF THE LIQUID-VAPOR EQUILIBRIUM IN THE BROMINE-HYDROBROMIC ACID-WATER SYSTEM

5. Report Date DECEMBER 1984

6. Performing Organization Code

7. Author(s)
R. Benizri, P. Lessart and P. Courvoisier
DCAEA/SCECF - CEN/SACLAY

8. Performing Organization Report No.

9. Performing Organization Name and Address
SCITRAN
Box 5456
Santa Barbara, CA 93108

10. Work Unit No.

11. Contract or Grant No. NASw- 4004

13. Type of Report and Period Covered
Translation

12. Sponsoring Agency Name and Address
National Aeronautics and Space Administration
Washington, D.C. 20546

14. Sponsoring Agency Code

15. Supplementary Notes

Translation of "Etude de l'equilibre de phases liquides-gaz dans le system brome-acide bromhydrique-eau". Communication of the European Communities. Report EUR 6783, 1980, Hydrogen Energy Vector, pp 101-116.

16. Abstract

A glass ebullioscope was built and a method developed to study, at atmospheric pressure, liquid-vapour equilibria relative to the Br_2-HBr-H_2O system, in the concentration range of interest for evaluation of the MARK 13 cycle. Measurements were preformed for the brome-azeotrope (HBr-H_2O) pseudo-binary system and for the ternary system at temperatures lower than 125° C and in the bromine concentration range up to 13% wt.

17. Key Words (Selected by Author(s))

18. Distribution Statement
Unclassified and Unlimited

19. Security Classif. (of this report) Unclassified

20. Security Classif. (of this page) Unclassified

21. No. of Pages 15

22. Price

STUDY OF LIQUID-GAS PHASE EQUILIBRIUM IN THE BROMINE-HYDROBROMIC ACID-WATER SYSTEM

1. INTRODUCTION

/102*

The "Mark 13" chemical decomposition cycle of water that was analyzed at the Centre d'Ispra (and set up in a laboratory loop operating continuously and producing 100 $l.h^{-1}$ of hydrogen) [1] includes 3 steps:

(1) $Br_2 + SO_2 + 2\ H_2O \longrightarrow H_2SO_4 + 2HBr$

(2) $H_2SO_4 + H_2O + SO_2 + \frac{1}{2}O_2$

(3) $2HBr + Br_2 + H_2$ (electrolysis)

To calculate the amount of energy needed to separate the bromine produced by electrolysis from the hydrobromic acid in the presence of water through distillation, and to determine the size of the corresponding columns, it is necessary to know the concentrations at the liquid-vapor phase equilibrium of the H_2O-HBr-Br_2 ternary system for certain ranges of interest for the process. As requested by the Ispra engineers, this equilibrium was studied at Saclay as part of a contract with the Commission of the European Communities (project H/A22).

A summary of the bibliographic study concerning the H_2O-HBr-Br_2 ternary system may be found in the reports from the preceding seminar on hydrogen organized by the CEC [2]. It is reminded that the liquid-vapor equilibrium diagram of binary system H_2O-HBr is known at atmospheric pressure [3]. The miscibility range of the pseudoternary bromine azeotrope (H_2O-HBr 47%) was defined at 20°C [4]; this is shown in Figure 1. The properties of the solutions formed by the 3 compounds were also studied in 5 .

In order to determine the liquid-gas phase equilibriums of ternary system Br_2-HBr-H_2O we built a glass ebullioscope and designed a procedure [2]. Measurements were taken at atmospheric pressure in the concentration range of interest for the Mark 13 process.

---

* Numbers in margin indicate foreign pagination.

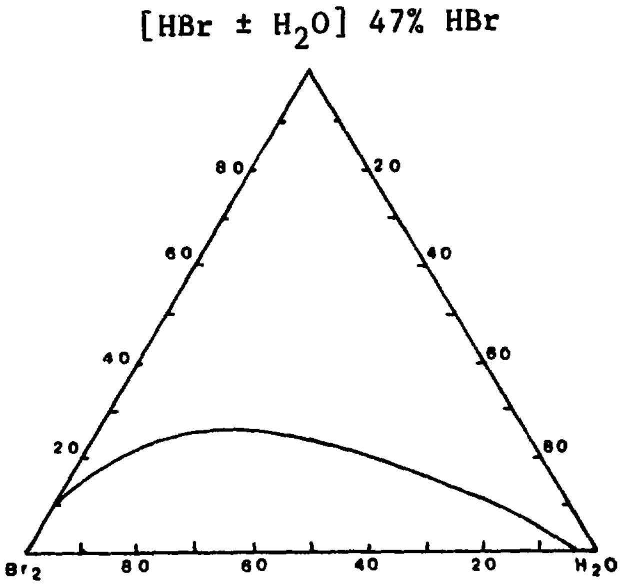

Fig. 1 - Miscibility diagram of pseudo-binary Br_2-HBr 47% - H_2O [4].

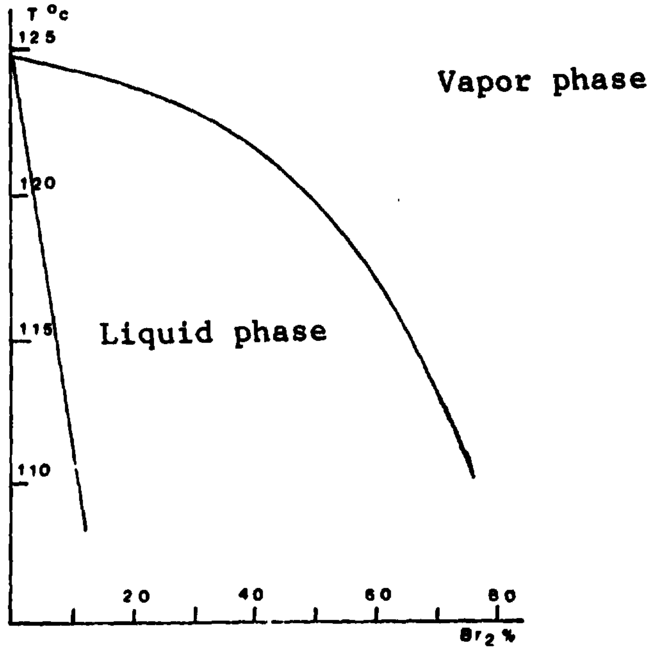

Fig. 2 - Liquid-vapor equilibrium diagram of pseudo-binary Br_2-HBr azeotrope at 760 mm Hg.

2. EBULLIOSCOPE AND MEASUREMENT THEORY

The ebullioscope has a dual function: first, it enables the liquid /104 and vapor phases to be put into equilibrium, with measurement of the temperature at fixed values of pressure; second, it enables the separation and taking of samples of the phases in equilibrium. The samples are then analyzed. The CATHALA ebullioscope [6] used is schematized in Figure 3. A preheated liquid and a superheated vapor flow into a mixer at a constant rate. The mixer is composed of two perforated plates and a COTTRELL nozzle equipped with VIGREUX points. The closely mixed liquid-vapor mixture wets a thermometric sheath before it completely separates into two phases which are cooled and condensed and then sent to the sampling outlets.

The instrument underwent a preliminary calibration to determine:

- The flow rates not to be exceeded in order to prevent droplets of liquid from being drawn along with the vapor;
- The amount of time the fluids remain in the space between the thermocouple sheaths and the bleed valves.

The various equilibrium points are studied by varying the supply flows, the temperatures, and the concentrations of the entering liquids.

Proper operation of the ebullioscope greatly depends upon the supply conditions.

The primary problems encountered were due to the highly active nature of the fluids studied. Only viton and teflon should be used for the flexible connections of the instrument. Beyond 100°C teflon does not withstand prolonged contact with the liquid phases.

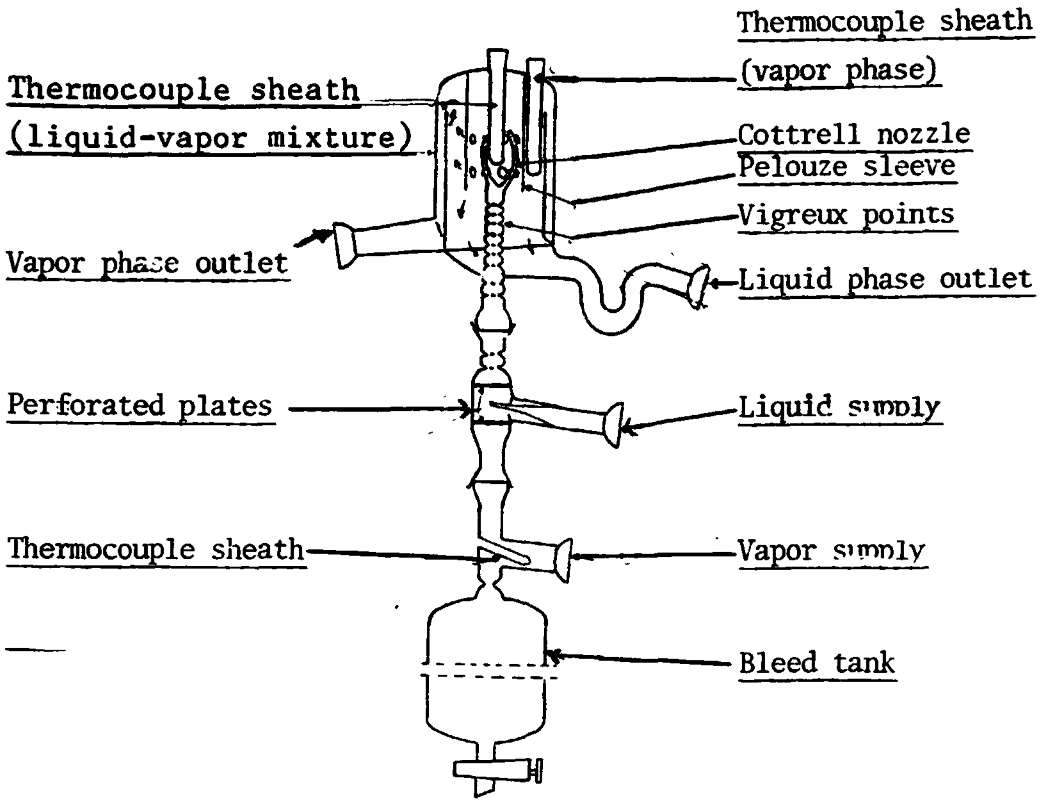

Fig. 3 - CATHALA ebullioscope

TABLE I

Densities of HBr - Br_2 - H_2O solution for varying values of normality N and temperature T

T°C	N_{HBr} eq. HBr/l	N_{Br_2} eq. Br/l	Density	HBr % mass	Br_2 % mass
20,7	8,04	3,53	1,653	39,30	17,06
20,8	6,04	12,93	2,104	23,40	49,47
21,6	8,44	1,91	1,584	43,12	9,62
21,6	7,22	7,71	1,865	31,56	33,28
22,4	4,81	3,66	1,487	26,24	19,72
20,6	7,95	4,02	1,682	38,33	19,14
20,6	5,70	5,33	1,634	28,30	26,14
20,6	5,50	7,95	1,776	25,14	35,89

3. DENSITIES OF SOLUTIONS

Proportioning of the liquid and vapor phases in equilibrium leads to determination of the number of moles of hydrobromic acid and bromine per liter of solution. These molarities are linked to mass percentages W by the densities of the corresponding solutions according to the following formulas: /106

$$W_{HBr} = \frac{8.092\ M_{HBr}}{d} \qquad W_{Br_2} = \frac{15.9808\ M_{Br_2}}{d}$$

where M represents the molar concentrations of HBr and Br_2 in the solution of density d.

We had first used density values evaluated according to documentation based on the empirical law: $d = A(N_{HBr} + N_{Br_2}) + B$, where A and B are constants and N_{HBr} and N_{Br_2} are normalities of the solution; density is expressed linearly depending on the total number of bromine equivalents contained in a liter of solution, with the bromine equivalents originating from the HBr or Br_2 having the same "weight".

For cross-checking purposes, and in order to more closely evaluate the mass percentages, we performed some experimental determinations of the density of the HBr - Br_2 - H_2O solutions. In order to do this we worked at ambient temperature using pycnometers whose volumes were determined at the temperature considered in relation to water at 4°C.

The results, according to the temperature and normality of the solutions, are given in Table I. Within the limits of experimental accuracy, our results agree with those of the existing documentation.

In addition, we calculated, through the method of the least squares, the equations that are likely to correlate with greater accuracy than the linear law, the densities given at 20°C by the documentation and the normalities of the bromine and hydrobromic acid solutions.

TABLE II

Experimental results for pseudo-binary mixture
Br_2 - azeotrope HBr, H_2O

	Liquid phase					Vapor phase				
T°C	Moles HBr/l	Moles Br_2/l	Density	HBr % mass	Br_2 % mass	Moles HBr/l	Moles Br_2/l	Density	HBr % mass	Br_2 % mass
123,6	8,70	0,0904	1,4986	46,98	0,964	7,80	2,2305	1,6954	37,23	21,02
123,4	8,62	0,1083	1,4962	46,62	1,16	7,74	2,635	1,7388	36,02	24,22
123,1	8,56	0,1337	1,4957	46,31	1,43	7,64	3,042	1,7803	34,73	27,31
122,3	8,68	0,173	1,5070	46,61	1,83	7,14	3,96	1,8587	31,08	34,04
121,8	8,58	0,204	1,5050	46,13	2,17	6,90	4,66	1,9265	28,98	38,65
121,3	8,59	0,269	1,5131	45,94	2,83	7,7	2,85	2,0840	29,89	43,27
120,5	8,64	0,288	1,5181	46,05	3,04	6,34	6,095	2,0618	24,88	47,24
120,1	8,63	0,3029	1,5192	45,97	3,18	6,22	6,197	2,0671	24,15	47,91
118,6	8,58	0,449	1,5332	45,28	4,68	5,36	7,55	2,1776	19,92	55,44
118,0	8,40	0,491	1,5280	44,48	5,13	5,25	8,125	2,2376	18,98	58,03
116,0	8,45	0,642	1,5482	44,16	6,63	4,3	10,03	2,4074	14,45	66,59
115,6	8,56	0,67	1,5576	44,47	6,87	4,26	10,41	2,4489	14,08	67,91
114,5	8,28	0,74	1,5504	44,22	7,65	4,07	10,94	2,5006	13,18	69,90
113,4	8,32	0,87	1,5674	42,95	8,87	3,79	11,83	2,5889	11,84	73,0
112,9	8,34	0,875	1,5690	43,01	8,91	3,68	11,687	2,5668	11,62	72,76
112,5	8,43	0,946	1,5828	43,11	9,56	3,51	11,875	2,5794	11,02	73,57

TABLE III

Experimental results for ternary system Br_2 - HBr - H_2O
range of low concentrations of bromine

T°C	Liquid phase					Vapor phase				
	Moles HBr/l	Moles Br_2/l	Density	HBr % mass.	Br_2 % mass.	Moles HBr/l	Moles Br_2/l	Density	HBr % mass.	Br_2 % mass.
124,7	8,70	0,0105	1,4894	47,27	0,112	8,55	0,195	1,5023	46,05	2,07
124,6	8,63	0,0120	1,4856	47,01	0,129	7,79	0,2326	1,4642	43,05	2,54
124,0	8,20	0,0217	1,4527	45,36	0,237	5,59	0,5145	1,374	32,92	5,98
124,0	8,68	0,0580	1,4937	47,02	0,620	7,78	1,423	1,6011	39,32	14,20
123,1	7,97	0,0397	1,4419	43,72	0,4399	3,90	1,306	1,3718	23,00	15,21
122,7	7,72	0,0224	1,4360	43,50	0,2493	2,72	0,5465	1,2117	18,07	7,17
122,3	7,80	0,0190	1,4401	43,83	0,2108	2,98	0,4945	1,2262	19,66	6,44
121,8	7,50	0,0297	1,4246	42,60	0,3332	0,53	0,5875	1,1001	3,89	8,531
119,9	7,09	0,0344	1 4022	40,91	0,3905	1,3	0,703	1,1568	9,09	9,71
118,1	6,68	0,0344	1,3798	39,19	0,398	0,79	0,6795	1,1257	5,68	9,65
117,4	6,70	0,0337	1,3803	39,28	0,390	0,68	0,711	1,1232	4,90	10,11
112,0*	5,44	0,0239	1,3088	33,63	0,292	0,110	0,161	1,0271	0,86	2,50
107,4*	4,22	0,0307	1,2415	27,51	0,395	0,025	0,099	1,0151	0,199	1,56

* Presence of another liquid phase with a high concentration of bromine when the vapor phase undergoes condensation.

TABLE IV

Experimental results for ternary system Br_2 - HBr - H_2O
Bromine concentration range greater than 1%

T°C	Liquid phase					Vapor phase					Point No.
	Moles HBr/l	Moles Br_2/l	Density	HBr % mass.	Br_2% mass.	Moles HBr/l	Moles Br_2/l	Density	HBr% mass.	Br_2% mass.	
122,5	8,27	0,133	1,4795	45,23	1,44	4,93	2,97	1,6227	24,58	29,29	1
121,6	8,22	0,180	1,4810	44,80	1,94	3,99	3,63	1,6468	19,60	35,22	2
121,1	7,90	0,193	1,4[illegible]7	43,61	2,10	2,98	3,82	1,6133	14,95	37,84	3
120,6	8,17	0,625	1,5309	43,21	6,52	3,89	9,75	2,3526	13,38	66,21	4
119,8	7,95	0,287	1,4794	43,48	3,10	1,50	5,14	1,6863	7,20	48,76	5
119,5	7,59	0,237	1,4535	42,25	2,60	2,12	4,06	1,5938	10,76	40,71	6
118,5	7,82	0,419	1,4874	42,54	4,50	2,27	7,06	1,9526	9,43	57,82	7
118,2	7,77	0,402	1,4826	42,41	4,33	2,62	6,45	1,9000	11,18	54,25	8
117,3	7,12	0,584	1,4336	40,18	3,25	1,07	5,16	1,6645	5,20	49,54	9
117,0	7,54	0,414	1,4712	41,47	4,49	0,6	6,81	1,8315	2,65	59,42	10
115,8	7,96	0,631	1,5196	42,38	6,63	2,84	7,71	2,0596	11,17	59,85	11
115,6	7,04	0,305	1,4307	39,81	3,41	0,77	5,67	1,7078	3,65	53,06	12
115,5	6,95	0,674	1,4294	39,34	3,77	0,82	5,66	1,7092	3,88	52,92	13
114,5	6,82	0,335	1,4213	38,81	3,76	0,52	5,82	1,7114	2,46	54,34	14
113,3	6,76	0,632	1,4529	37,65	6,95	1,64	7,67	1,9894	6,69	61,65	15
112,9	7,58	0,826	1,5210	40,33	8,68	1,47	9,86	2,2349	5,32	70,50	16
112,5	6,54	0,398	1,4129	37,45	4,44	0,39	5,94	1,7191	1,84	55,26	17

TABLE IV (Cont'd)

Experimental results for ternary system Br_2-HBr-H_2O
Bromine concentration range greater than 1%.

T°C	Liquid phase					Vapor phase					Point No.
	Moles HBr/1	Moles Br_2/1	Densité	HBr % mass.	Br_2% mass.	Moles HBr/1	Moles Br_2/1	Densité	HBr % mass.	Br_2% mass.	
111,2	6,55	0,580	1,4357	36,92	6,51	0,41	7,94	1,9541	1,72	64,97	18
108,7	5,48	0,400	1,3552	32,72	4,77	0,08	6,50	1,7728	0,04	59,04	19
108,7	7,03	1,280	1,5431	36,86	13,27	0,61	12,03	2,4427	2,02	78,74	20
107,1	5,60	0,517	1,3749	32,96	6,01	0,08	7,16	1,3431	0,37	61,99	21
105,3	4,79	0,335	1,3049	29,70	3,72	0,032	5,38	1,6338	0,16	52,67	22
104,2	3,14	0,182	1,1987	21,19	2,43	0,15	3,82	1,4573	0,83	41,89	23
104,0	3,95	0,258	1,2528	25,51	3,29	0,02	6,01	1,7064	0,09	56,29	24
104,0	4,97	0,571	1,3460	29,88	6,78	0,05	7,36	1,8662	0,20	63,07	25
103,8	5,45	0,749	1,3934	31,65	8,59	0,04	8,9	2,0516	0,18	69,72	26
102,0	3,01	0,161	1,1890	20,48	2,16	0,01	3,59	1,4160	0,03	39,89	27
100,7	2,50	0,151	1,1595	17,44	2,09	0,004	3,64	1,4282	0,02	40,73	28
100,2	3,76	0,496	1,2699	23,96	6,24	0,04	7,11	1,8370	0,20	61,89	29
99,1	2,36	0,256	1,1638	16,40	3,51	0,03	4,91	1,5789	0,17	49,74	30
97,8	3,48	0,664	1,2738	22,11	8,33	0,06	8,20	1,9648	0,25	66,69	31

It appears that the best correlation is of the following type:

$$d = A.N_{HBr} + B.N_{Br_2} + C.N_{HBr}.N_{Br_2} + D$$ /111

In this formula the bromine equivalents no longer have the same influence, depending on whether they come from hydrobromic acid or bromine; nevertheless their respective "weights" are very similar, with constants A and B being very close. For information purposes the values of the constants are as follows:

$A = 5.5859\ 10^{-2}$ $B = 5.8489\ 10^{-2}$

$C = -9.7082\ 10^{-5}$ $D = 1.0012$

4. EXPERIMENTAL RESULTS

The results of the ebullioscope measurements for the pseudo-binary mixture of Br_2-azeotrope (HBr-H_2O) are grouped together in Table II and represented in Figure 2. The experimental results of the phase equilibrium study for ternary system Br_2-HBr-H_2O are shown in Table III for small concentrations of bromine and in Table IV for larger concentrations.

The experimental points of Table IV were located in a [illegible]ry diagram: in Figures 4 and 5 the points bearing the same numbers (defining the experiment - refer to Table IV) correspond to the phases in equilibrium; the points represented by circles give the composition of the vapor phase, whereas those represented by a cross give that of the liquid phase. As for Table III, the proximity of the [illegible]rimental points makes any representation on a ternary diagram impossible.

The compositions of the liquid and vapor phases in equilibrium are shown for different temperature values T (°C) (first column). The results given in the other columns are described as follows:

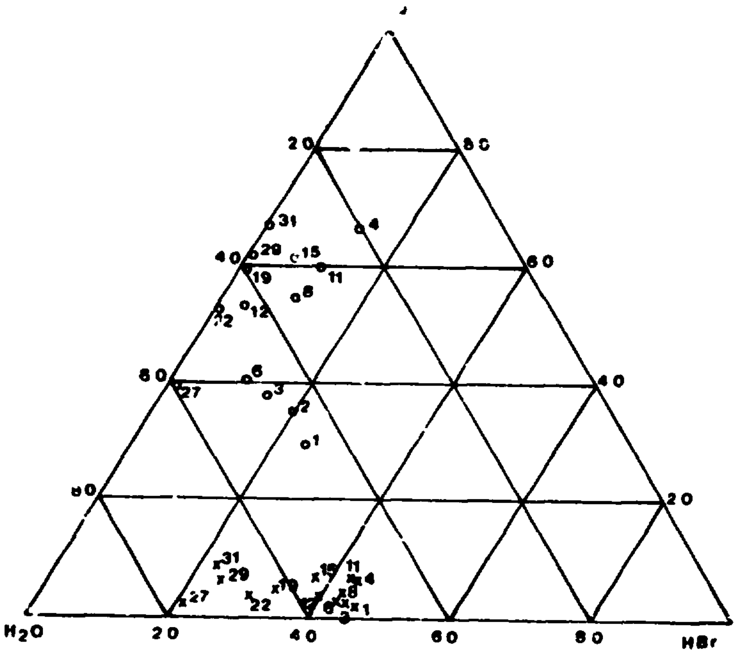

Fig. 4

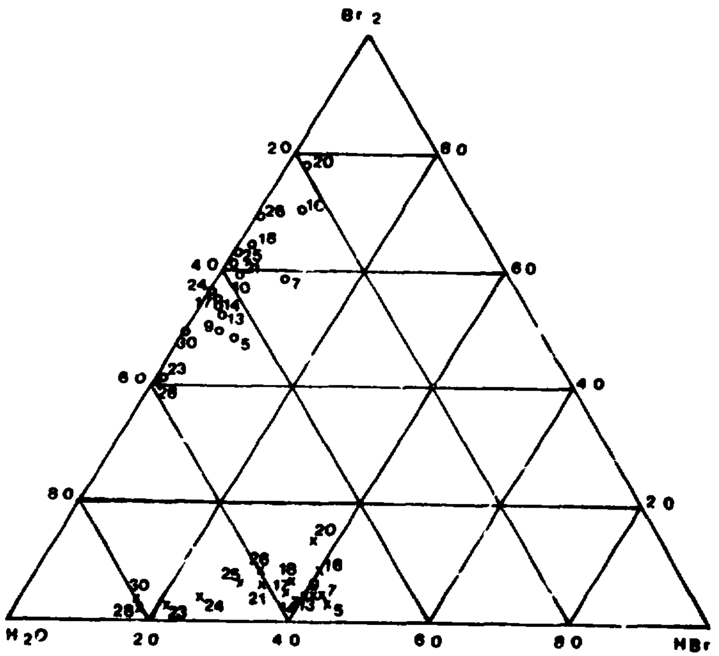

Fig. 5

Ternary diagram of H_2O-Br_2-HBr for the range of bromine concentrations greater than 1% in the liquid phase.

o - Compositions of vapor phases in mass %

x - Compositions of liquid phases in mass %

An identical reference number corresponds to a phase equilibrium (refer to Table IV).

- "Moles HBr/l" represents the molarity of HBr in the liquid or vapor phase at ambient temperature. This molarity is obtained by metric acid-base pH proportioning. /113

- "Moles Br_2/l" represents the molarity of Br_2 in the liquid or vapor phase at ambient temperature. This molarity is obtained by potentiometric oxydation-reduction proportioning of iodine by sodium hyposulfite according to the following reaction:

$$2\ S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2\ I^-$$

The bromine, which is a stronger oxydizer than iodine, oxydizes the thiosulfate into sulfate under variable conditions. This is why the proportion of bromine is controled by adding excess KI before titrating the released iodine with thiosulfate

$$Br_2 + 2\ I^- \longrightarrow I_2 + 2Br^-$$

In a very acid environment, since the iodine can be oxidized by the oxygen in the air, proportioning is performed in an argon atmosphere and in a solution adjusted to a pH number of 5 (acetate solution).

"Density" represents the mass per unit volume in g/cm^3 of the liquid or vapor phases at ambient temperature.

"HBr mass %" represents the mass of HBr contained in 100 grams of solution, either in the liquid or vapor phase, at ambient temperature.
This value is calculated using the molar mass of HBr, the molarity determined experimentally, and the density evaluated according to the documentation.

"Br_2 % mass" likewise represents the weight titre of the solution in Br_2.

The concentrations of HBr and Br_2 given for the vapor phase represent an average concentration of two liquid phases generally obtained after condensation of the vapor. The maximum concentration obtained for the liquid phase does not exceed 13.3 % bromine /114

5. DISCUSSION

In the course of this work about sixty different liquid-vapor phase equilibrium points for the HBr-Br_2-H_2O system were determined for the corresponding temperatures. However, only a limited area of the ternary diagram was explored.

If one wished to extend the study of this diagram, two major difficulties would be encountered: the existence of a vast zone of partial mixing in the liquid phase and the extremely corrosive nature of the products.

Since the gaseous phase in equilibrium with the liquid phase is very rich in bromine, in order to extend the realm of study it would be necessary to modify the Cathala ebullioscope to enable injection of a liquid phase having a similar composition to that desired, as well as two gaseous phases in suitable proportions - one rich in Br_2 and therefore very poor in HBr and H_2O, the other very poor in Br_2 and with an HBr concentration such that, when the two gaseous phases are mixed, a gas of similar composition to that of the gaseous phase in equilibrium with the added liquid phase is obtained. In this case the Cathala ebullioscope would be equipped with a preheated-liquid input and two quartz atomizers with different heating capacities. The input lines should be welded to avoid having couplings in the hot zone. The other products should be supplied without pulsations by a nonvermicular proportioning pump; flexible lines are quickly deteriorated by concentrated bromine solutions (in some of the experiments the hoses were damaged in less than 6 hours).

6. CONCLUSION

As part of the studies concerning the cyclical Mark 13 process of hydrogen production, the isobaric diagram of liquid-vapor equilibrium for the Br_2-HBr-H_2O system was analyzed at atmospheric pressure and at temperatures greater than 300 K. The concentration range studied, which is of interest for the process, is limited by a large range of partial mixing of the system at ambient temperature and by the aggressive nature of the mixtures. Another ebullioscope would have to be designed to complete analysis of the system. /115

After careful examination of the results, observations concerning the separation of bromine, hydrobromic acid, and water after electrolysis, may be made (step 3 of the cycle - refer to §1). As the gaseous phase in equilibrium is very rich in bromine when compared to the liquid phase, separation should be easy and energy consumption moderate provided it is acceptable that the hyrobromic acid recycled into electrolysis still contain a little bromine at a concentration of a few thousandths. However, elimination of this small amount of bromine appears to be difficult, especially as the composition of the mixture becomes similar to that of the azeotrope HBr-H_2O.

REFERENCES

(1) D.VAN VELZEN et al.
Proceedings of the 2nd World Hydrogen Energy Conference.
Zurich. p.649, vol. 2, 1978.

(2) P. LESSART, R. BENIZRI
SEMINAR ON HYDROGEN AS AN ENERGY VECTOR. Bruxelles 1978.
p. 71 - Rapport EUR 6085 DE/EN/FR/IT

(3) E. CARRIERE and CERVEAU
Comptes Rendus Academie des Sciences, Vol. 177, pp 46-48, 1923

(4) M.A. MENKOVSKII, N.A. PETROU, K.I. LITVIN
J. of Inorganic Chemistry. USSR. vol. I, No. 7, 1956,
pp. 1658-64.

(5) W. GLASS
Hydrogen-bromine fuel cell
AFCRL-65-34, 1964.

(6) J. CATHALA
Ebullioscopy, Annales du Genie Chimique, II, PRIVAT, 1963.