# S-I thermochemical cycle for H<sub>2</sub> production: a thermodynamic analysis of the phase equilibria of the system HI-I<sub>2</sub>-H<sub>2</sub>O

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It is widely agreed that the most energy consuming part of the S-I thermochemical cycle for hydrogen production is represented by separation processes, especially for the HI decomposition section. The design of these processes and consequently the assessment of the real potential of the S-I cycle depends on the understanding of thermodynamic equilibrium and models construction of the ternary system HI-H<sub>2</sub>O-I<sub>2</sub>. In this paper, a new thermodynamic model for the electrolyte system HI-I<sub>2</sub>-H<sub>2</sub>O is proposed and validated against vapour-liquid (V-L) equilibrium data at atmospheric pressure. The proposed model provides a reliable description of V-L equilibrium of the ternary system of interest.

# **1. Introduction**

At present large scale and cost effective hydrogen production is obtained from fossil based processes, but the steady increase of fossil fuels price and the uncertainties of their long-term availability, along with the environmental alarm due to the greenhouse gas emissions, have promoted research work on the utilization of alternative energy sources. With this respect the thermochemical processes which produce hydrogen from water-splitting are very attractive, especially if they are powered by renewable primary energy sources. The thermochemical cycles, indeed, achieve water splitting through a series of chemical reactions, being the net result the production of hydrogen and oxygen at much lower temperatures than direct thermal decomposition. The S-I cycle currently represents the most promising candidate for hydrogen production among several alternatives proposed in the literature over the last 20 years. It basically consists of the following three chemical reactions, carried out at three different temperature levels (low, medium and high temperature):

- Bunsen reaction (exothermic at 20-120°C):

$$2H_2O + I_2 + SO_2 \rightarrow H_2SO_4 + 2HI \tag{1}$$

- Hydriodic acid decomposition (endothermic, at 300-450°C):

$$2HI \rightarrow I_2 + H_2 \tag{2}$$

Sulphuric acid decomposition (endothermic, at 800-900°C):

$$H_2SO_4 \rightarrow H_2O + SO_2 + \frac{1}{2}O_2 \tag{3}$$

The HI decomposition section  $(HI_x)$  has been identified as the key part for cycle optimization, since the presence of a homogeneous azeotrope in the binary system HI- $H_2O$  makes the HI concentration and subsequent decomposition very energy expensive. As a result some process solutions have been proposed and investigated, especially with respect to energy demand (Table 1): reactive distillation (Roth et al., 1989; Goldstein et al., 2005), membrane dissociation in conjunction with electrodialysis (Kasahara et al., 2004),  $H_3PO_4$  based scheme (O'Keefe et al., 1982). However, as current performance projections are based on uncertain and incomplete data, thermodynamic measurements and modelling for the  $HI_x$  section have been identified as a central research issue for the correct assessment of the  $HI_x$  energy demand and, consequently, of the whole S-I cycle true potential.

This work focuses on modelling of phase equilibria relevant to the HI decomposition section, in order to perform reliable mass and energy balances of the separation processes. As a first step, the model range of application has been restricted to the V-L equilibrium conditions, essential for thermal separation processes design. The tool used for the experimental data regression and process simulation is Aspen  $Plus^{TM}$  of Aspen Tech, currently adopted by different research groups working on S-I cycle development. In the following paragraphs at first a brief description of the thermodynamic system is presented, then the model development and the obtained results are reported. Finally the implemented model is validated on the basis of experimental data collected at the ENEA laboratories.

# 2. Description of the HI-I<sub>2</sub>-H<sub>2</sub>O system

The ternary system HI-I<sub>2</sub>-H<sub>2</sub>O involved in the hydriodic acid decomposition, shows a complex behaviour because of the various ionization and complexation phenomena that occur. In the liquid phase the solution chemistry is mainly represented by the electrolytic dissociation of HI in water (HI + H<sub>2</sub>O  $\leftrightarrow$  H<sub>3</sub>O<sup>+</sup> +  $\Gamma$ ) with the possible formation of some polyiodine complexes like the ionic species I<sub>3</sub><sup>-</sup> (Calabrese and Khan, 2000). This mechanism is supported by the fact that iodine has a strong affinity for aqueous solutions of hydrogen iodide, although it is only sparingly soluble in pure water. Due to the low solubility of iodine in water and the presence of a miscibility gap in the HI-H<sub>2</sub>O binary system, the ternary system exhibits liquid-liquid (L-L) equilibrium too (Norman, 1984). In the vapour phase the thermal HI decomposition into I<sub>2</sub> and H<sub>2</sub> was investigated by Berndhauser and Knoche (1994), who highlighted the strict dependency of the reaction yield upon the liquid HI degree of concentration.

Table 1: Calculated energy demand

Reference	Process solution	Calculated energy demand (kJ/mol <sub>H2</sub> )
Roth et al. (1989)	Reactive distillation	237
Brown et al. (2003)	Reactive distillation	245.8
Kasahara et al. (2004)	Electrodialysis	103.5-584.8
Goldstein et al. (2005)	Reactive distillation	375.0-454.0



Fig. 1: Neumann solution chemistry



The thermodynamic model assumed by many research groups (Goldstein et al., 2005; Elder et al., 2005) for the ternary system is the one proposed by Neumann (1987), in which a solvation reaction is taken into account in the liquid phase ( $nH_2O + HI <->$  [( $nH_2O,H^+$ ) $\Gamma$ ]), while in the vapour phase the HI decomposition equilibrium is considered, as shown in Fig. 1.

As a matter of fact this hypothesis significantly simplifies the model development, since no charged species are considered in the liquid phase and the activity coefficient model adopted is only based upon the short range interactions between molecules (NRTL, Renon (1968)). The fitting parameters of this kind of model are principally the molecule-molecule interaction terms and the number of hydration n. According to Goldstein et al. (2005), the phase diagrams can be calculated with accuracy on the lefthand side of the binary HI-H<sub>2</sub>O azeotrope and when the iodine content is low. Nevertheless, so far there is no experimental evidence of this hydration chemistry and therefore in this work the electrolytic dissociation of HI has been assumed (Fig. 2), taking into account the possible mechanism of partial dissociation, which can be significant for many electrolytes at high concentration (Chen et al., 1999). The formation of the  $I_3$  species is, at the moment, neglected, assuming the HI dissociation more relevant for the system behaviour description.

Regarding the model development, it is firstly necessary to analyse and collect data for each binary subsystem. For this reason, in Table 2, the experimental data available in literature for each sub-system are reported along with the indication of the reference, the phase equilibrium type and the range of operating conditions.

System	Exp. data	Data sources	Data number	T(K) range	Composition range (mole %)	Regressed data	Average error %
I <sub>2</sub> -H <sub>2</sub> O	S-L	Kracek 1931	13	273-379	$0.001 < x_{12} < 0.04$	Yes	0.0
	L-L	Kracek 1931	9	385-459	-	Yes	2.3
I <sub>2</sub> -HI	S-L	O'Keefe 1980	4	573-636	7.6 <x12<57.7< td=""><td>Yes</td><td>0.0</td></x12<57.7<>	Yes	0.0
$HI-H_2O$	V-L	Neumann 1987	75	350-553	$0 < x_{HI} < 19.4$	Yes	9.0
	V-L-L	Haase 1963	2	298-410	-	No	-
	V-L az	CRC 1976	1	126.5	$x_{HI} = 15.7$	Yes	7.8
	V-L	Sako 1985	30	273-399	$0.6 < x_{HI} < 16.7$	No	-
HI-I <sub>2</sub> -H <sub>2</sub> O	V-L	Neumann 1987	281	373-558	$0.33 < x_{12} < 85.6$	Yes	8.8
	L-L	Norman 1984	12	343-425	-	No	-

Table 2: Experimental data available

Concerning the I<sub>2</sub>–H<sub>2</sub>O mixture, the system is highly non ideal with L-L equilibrium exhibited above the melting point of iodine, while the HI-I<sub>2</sub> system is characterized by only small deviations from ideality. The electrolytic binary HI-H<sub>2</sub>O presents an homogenous azeotrope ( $X_{HImol}$ =0.157) and a L-L equilibrium above 0.3 HI mole fraction.

# 3. Model development

The selected thermodynamic model uses the RK equation of state for the calculation of the gas phase fugacity, while for the liquid phase it employs the electrolyte-NRTL activity coefficient model (Chen et al. 1982; Chen et al, 1986). The unsymmetric Pitzer-Debye-Hückel model (Pitzer et al., 1980) and the Born equation are used to represent the contribution of the electrostatic energy, while the Non-Random Two Liquid theory (Renon et al., 1968) is assumed to represent the short range interactions.

The model adjustable parameters basically are the molecule-electrolyte interaction parameters  $\tau_{ca,m}$  and  $\tau_{m,ca}$  and, for each binary sub-system, the molecule-molecule interaction parameters  $\tau_{m,n}$  and  $\tau_{n,m}$ . Since the temperature range of the experimental data is wide, the following temperature dependency of the interaction parameters has been assumed:

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} + e_{ij} \left( \frac{T^{ref} - T}{T} + \ln \frac{T}{T^{ref}} \right)$$

$$\tag{4}$$

As far as the binary HI-H<sub>2</sub>O is concerned, particular attention has to be paid to the choice of the species reference state. In order to describe the V-L equilibrium in a wide range of composition and possibly extend the model to the liquid-liquid equilibrium, the Raoult reference state has been chosen for HI. Since this state is a hypothetical state above the HI critical temperature (151.85°C), this assumption implies the extrapolation of the HI pure liquid volume  $V_L^o$  and the HI vapour pressure  $p_s(T)$  up to the highest temperature of interest.

As for the HI molar volume, an empirical correlation has been used which provides a constant value above the HI critical temperature. Details on the empirical correlation are reported elsewhere (Annesini et al., 2007).

In a similar way an empirical correlation also for  $p_s(T)$  has been introduced. The correlation parameters have been obtained anchoring the function to the experimental vapour pressure data (Aspen Plus Database) below the critical temperature and fitting multicomponent vapour-liquid data above the critical point (see next paragraph).

#### 4. Results

The regression of the model parameters listed in Table 3 has been performed on the basis of the experimental data summarized in Table 2, using the Maximum Likelihood method. In details, at first the binary systems  $I_2$ -HI and  $I_2$ -H<sub>2</sub>O was correlated; subsequently the simultaneous fitting of the binary HI-H<sub>2</sub>O and the ternary HI-H<sub>2</sub>O-I<sub>2</sub> was carried out along with the evaluation of the HI vapour pressure.

Interaction parameters				HI vapour pressure					
System	Parameter	Coefficients (SI units)				Coefficients (atm)			
		a	b	e	Α	В	С	D	Е
$I_2$ - $H_2O$	$\tau_{\rm I2,H2O}$	-5.14	3320.94	0.00	45.32	-3389.51	0,00	0,0081	-6.03
	$\tau_{I2,H2O}$	-3.80	3959.40	0.00					
I <sub>2</sub> -HI	$\tau_{I2,HI}$	0.00	4510.90	0.00					
	$\tau_{I2,HI}$	0.00	-1586,06	0.00			D		
$HI-H_2O$	$\tau_{\rm H2O-(H3O+I-)}$	19.11	-4104.22	-9.49	$\ln p_s = A + \frac{B}{C + T} + D \cdot T + E \ln T$				hT
	$\tau_{(H3O+I-)\text{-}H2O}$	-0.17	1277.09	14.13		(	, T <b>I</b>		
HI-I <sub>2</sub> -H <sub>2</sub> O	$\tau_{I2\text{-}(H3O\text{+}I\text{-})}$	10.34	673.24	0.00					
	$\tau_{(H3O+I-)-I2}$	-8.05	1909.28	0.00					

Table 3: Regressed parameters

Finally, using as initial guesses all the values obtained by the previous fittings, an overall parameters regression was performed in order to refine the calculation.

The resulting parameters values are presented in Tables 3, while the average error relative to each experimental data set is shown in Table 2. The model provides a fair description of the V-L equilibrium behaviour with an absolute average error lower than 10%. However it is worth noting that the highest deviations between experimental and calculated pressure occur at high  $I_2$  concentrations and at hyperazeotropic compositions.

# 5. Model validation

An experimental campaign for acquiring  $HI-I_2-H_2O$  VLE data has been launched, with the aim of enhancing the thermodynamic knowledge of the phase equilibria. As a first step, the initial boiling temperature of the binary  $HI-H_2O$  and the vapour equilibrium composition have been detected. Measurements have been performed at atmospheric pressure by means of a recirculating ebulliometer varying the HI mole fraction within the range 0-0.22. The experimental procedure and the apparatus used are reported elsewhere (Capparucci et al., 2007).



Fig. 3: HI-H<sub>2</sub>O V-L eq. prediction compared with experimental data (P= 1 atm)

In Fig. 3 the HI-H<sub>2</sub>O phase diagram at atmospheric pressure predicted by the model is shown along with the experimental data collected so far.

### 4. Conclusions

In the present study a thermodynamic model for the  $HI-I_2-H_2O$  ternary system has been developed. The model correctly accounts for the electrolytic chemistry and reasonably describes the V-L equilibrium behaviour. So far the possible formation of the ionic complex  $I_3^-$  has not been included in the solution chemistry but it could enhance the response of the model at high  $I_2$  concentration. For this reason further analysis will be undertaken in order to investigate the effect of the introduction of the species  $I_3^-$  upon the phase equilibria description. Moreover an additional study dealing with thermal effects will be carried out for improving the accuracy of energy balances calculation.

#### 5. References

- Annesini M.C, F. Gironi, M. Lanchi, L. Marrelli and M. Maschietti, 2007, Report ENEA/SOL/RS/2007/05.
- Berndhauser C. and K. Knoche, 1994, Int J. Hydrogen Energy, 244, 19.
- Brown L.C., JF Funk and SK. Showalter, 2003, Report GA A23373.
- Calabrese V. T. and A. Khan, 2000, J. Phys. Chem., 1287, 104.
- Capparucci C., A. Ceroli, M. Lanchi and R. Liberatore, 2007, Report ENEA/SOL/RS/2007/04.
- Chen C.C., H.I. Britt, J.F. Boston and L.B. Evans, 1982, AIChE Journal, 588, 28.
- Chen C.C. and L. B Evans., 1986, AIChE Journal, 444, 32.
- Chen C.C., P. Mathias. and H. Orbey, 1999, AIChE Journal, 1576, 45, 7.
- CRC Handbook of Chemistry and Physics, 1975, 56th Edition, CRC Pres.
- Elder R.H., G.H. Priestman, B.C. Ewan and R.W.K. Allen, 2005, Trans. IChemE, Part B, Process Safety and Environmental Protection, 343, 83(B4).
- Goldstein S., J.M Borgard and X Vitart., 2005, Int. J. Hydrogen Energy, 619, 30.
- Haase R., H. Naas and H. Thumm, 1963, Z. Phys. Chem. NF, 37, 210.
- Kasahara S., S. Kubo, K. Onuki and M. Nomura, 2004, Int J. Hydrogen Energy, 579, 29.
- Kracek F. C., 1931, J. Phys. Chem., 35, 417.
- Neumann Dirk, 1987, Phasengleichgewichte von HI/H2O/I2-Losungen, Thesis, Lehrstuhl fur Thermodynamic, RWTH Aachen (in German).
- Norman J. H., 1984 (unpublished data).
- O'Keefe D. R.and J. H.Norman, 1980, J. Chem. Eng. Data, 77, 27.
- O'Keefe D., C. Allen, G. Besenbruch, L. Brown, J. Norman and R. Sharp, 1982, Int J. Hydrogen Energy, 381, 7, 5.
- Renon H. and J.M. Prausnitz, 1968, AIChE Journal, 14,1.
- Roth M. and K.F. Knoche., 1989, Int J. Hydrogen Energy, 545, 14, 8.
- Sako T., T. Hakuta, H. Yoshitome, 1985, Kagaku Gijutsu Kenkyusho Hokoku, 199, 80.