and heat of mixing for the Zn-Cd-Sn ternary solution, respectively.

$$F^{xs} = (2370 + 1.354T) N_{Cd} [1 - (1 - N_{Zn})^{0.54}] + (2180 - 1.655T) N_{Sn} [1 - (1 - N_{Cd})^{0.86}] \\ + (-4750 + 29.35T) N_{Sn} [1 - (1 - N_{Zn})^{-0.04}] \\ \Delta H = 2370 N_{Cd} [1 - (1 - N_{Zn})^{0.54}] + 2180 N_{Sn} [1 - (1 - N_{Cd})^{0.86}] - 4750 N_{Sn} [1 - (1 - N_{Zn})^{-0.04}] \\ S^{xs} = -1.354 N_{Cd} [1 - (1 - N_{Zn})^{0.54}] + 1.665 N_{Sn} [1 - (1 - N_{Cd})^{0.86}] - 29.35 N_{Sn} [1 - (1 - N_{Zn})^{-0.04}]$$

The excess free energy calculated from the relation is in good agreement with the experimental results, but the calculated values have considerable discrepancies for the excess entropy and the heat of mixing.

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Studies on the Preparation of Fluorine and Its Compounds.

I. Manufacturing Equipments of Anhydrous Hydrofluoric Acid and 100 Amp. Fluorine Cell

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Fluorine is the most active of elements. It is used not only for the isotope separation of uranium in the form of uranium hexafluoride, but also for the preparation of fluorine compounds including fluorinating agents. It is only in relatively recent years that there has been any commercial demand for element fluorine, and therefore the studies on the preparation of fluorine and its derivatives, particularly anode phenomena during electrolysis and the mechanisms of the reaction processes of the fluorination etc, have not been fully investigated. From these points of view, we have dealt with and discussed our present problems.

The equipment for manufacturing anhydrous HF consisting of a gaseous HF generator with a rotating rod, a dust chamber, three cooling towers and three reservoirs have been designed. As reagents, concentrated sulfuric acid (98%) and commercial fluorspar (purity 97%) were used, that is, 200 g of fluorspar and sulfuric acid were set into the generator and the mixture was agitated with the rotating rod. The HF gas generated was first passed through the dust chamber to remove dusts, sulfuric acid, fluorosilicate compounds, water, etc. Then, it was passed through the first cooling tower, where the other impurities, for example,

Fig. 1 Liquid anhydrous fluorine acid generater and its additional equipment

azeotropes, were condensed. In the second cooling tower, the hydrofluoric acid was pre-cooled and in the last tower it was perfectly condensed into the reservoir as the liquid state.

A fluorine cell of 100A scale was designed and operated. The inner construction of the fluorine cell is shown in Fig 2. Several carbon rods (6 cm in diameter and 50 cm in length) were used as anodes, and the anode area was about 7.4 dm². The cathode of 8 meshes iron net was welded with three iron rods (8 mm ϕ) and insulated from the cell's steel cover with a Teflon packing. The diaphragm of copper, of which lower portion is an iron screen was used. An oil jacket of mild steel had a coiled cooling pipe, through which cooling water passes. The heat medium was liquid paraffin and the capacity of the bath was about 18 l. The cell body which is made of mild steel can be charged with 15 l of the electrolyte. The cell cover carries a hydrogen outlet pipe, a hydrofluoric acid feed line, a thermocouple well, a fluorine outlet pipe and an electrolyte sampling pipe, etc. The composition of the electrolyte was varied from KF. 1.86 HF to KF. 2.2 HF. 1.0 to 2.0 wt% of lithium fluoride was often added to the electrolyte. The cell was operated at 70~110°C with a carbon or a nickel anode alone at low current densities under below 3V until the water was removed, after thereafter normal operation could be resumed.

Fig. 2 Fluorine cell

Experimental Results

The best condition was studied through operations at different heating temperatures of the generator,

Table 1 Data of the Anhydrous Fluoric Acid Preparation

Dropping time of sulfuric acid min (5cc/min)	Temp. of gases at the tops and bottoms of the condensers (°C)						Temp. in HF generator (°C)	Temp. of generated gas (°C)	Press. in the reactor (mmHg)	Number of leaking bubbles due to incomplete condn. (Number of bubble/min)
	cond. 1		cond. 2		cond. 3					
	top	bottom	top	bottom	top	bottom				
9	29.0	38.0	11.2	12.0	9.5	9.0	120	44	35	14
10	37.0	39.0	11.2	11.9	9.5	9.0		50	80	20
20	54.2	46.1	29.0	19.0	9.7	9.0		56	50	31
30	57.0	52.0	32.8	24.0	14.2	9.0		65	35	10
40	55.0	49.9	33.2	26.2	20.8	9.0		83	80	0
50	56.0	52.8	33.2	27.0	24.8	9.3	180	90	75	0
60	56.0	53.0	30.9	25.0	24.8	9.7		108	77	0
70	51.0	49.0	26.1	23.0	20.0	9.7		113	75	0
80	46.0	42.8	22.0	20.0	17.2	9.7		113	55	0
90	50.0	42.7	19.0	18.0	16.9	9.5		116	10	0
100	44.0	42.0	18.0	17.0	11.2	9.2		121	5	26
110	42.0	41.8	16.0	16.0	10.9	9.0		118	3	30
120	45.0	44.8	15.0	15.0	10.5	9.0		110	3	43
temp. of cooling water HF purity air cooling	about 42°C 63.2% 55g		air cooling 11°C 97.2% 27g		about 8°C 99.0% 163g		dust chamber 53.7% 21g			
materials	Silica (medical use) 600g, conc. sulfuric acid (98%) 650cc									
over-all yield	87.5%

Fig. 3 Potential-current curve characteristics of the fluorine cell

Fig. 4 Potential-current characteristics of the fluorine cell (2.0 wt./LiF added)

different cooling temperatures and different rates of dropping sulfuric acid. One of these results is given in Table 1.

The voltage drops from anode to electrolyte, from electrolyte to cathode and from anode specimen to cathode specimen, as well as the over-all cell voltage are shown as a function of the current densities in Figs. 3 and 4. The voltage drop from anode to electrolyte seems to be distinctly greater than that from electrolyte to cathode, and the contribution due to the resistance of the electrolyte increases linearly with increasing current density. As shown in Fig. 3, anode effect suddenly appeared at about 9 A/dm². This anode polarization could be decreased by two of our empirical treatments: the addition of 2% of lithium fluoride to the electrolyte, and the elimination of the water in electrolyte by means of electrolysis with a nickel anode.

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Electrolytic Reactions of ω -Amino Compounds and Their Acyl Derivatives. V. Electrochemical Oxidations of ω -Amino Acids and Their Lactams*

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1. Introduction

From the principles underlying the conclusions of the previous papers (part I-IV)¹⁾ reported by the author, it may be assumed that the lactams (the intramolecular N-acyl compounds of ω -amino acids) are also easily oxidized electrochemically in sulfuric acid solution. The author had already studied the comparative electrochemical oxidations of the simple lactams with their parent ω -amino acids and had obtained the analogous results that the lactams (I) had undergone oxidation readily with the formations of their corresponding dicarboxylic acid imides (II) as their first intermediates.

Thus, α -pyrrolidone (γ -butyrolactam) gave succinimide (59 mol % yield), α -piperidone (δ -valerolactam) glutarimide (43 mol%) and unknown black dyestuff (17 wt%), and ϵ -caprolactam adipamic acid (13 mol %)

* Reported at the 5th (Apr. 1952, in Tokyo), 6th (Apr. 1953, in Kyoto) and 8th (Apr. 1955, in Tokyo) annual meeting of the Chem. Soc. of Japan.

The original written in Japanese can be seen in *Denki-Kagaku* 29, 290 (1961).