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## ON THE ADSORPTION OF HYDROCYANIC ACID ON ELECTRODES

By

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### Abstract

The interface Hg/0.1 N HCl aq.+various amounts of HCN was studied by the electrocapillary method and by differential capacity measurements. The results of the first method indicate absence of adsorption over the entire potential range. The results of the latter indicate zero adsorption at negative charges on the metal, but non-zero adsorption at positive charges. The magnitude and the shape of the isotherm of HCN adsorption differ widely for different ways of evaluation.

Three checks are applied to the results: (a) Physical significance, (b) Comparison with the predictions of theories concerning the variation of adsorption with the electric variable and concerning the magnitude of interfacial tension, (c) Fit to a mechanism with which to explain the well-known catalytic poisoning action of HCN.

A model of the adsorption of HCN is put forward which, on the basis of these checks, leads to a reasonable description of the observations on adsorption and differential capacity. According to this model, HCN has an exceptional adsorption behaviour; it becomes adsorbed at the sites of ions in contact with the electrode, displacing them from the electrode surface.

### Introduction

Hydrocyanic acid is among the substances which exert a highly poisonous action on catalysts. Its adsorption from solution, however, seems not to have been studied much although it is of interest in several respects: (a) In connection with both the active centre theory and the crystal plane model of catalysts (its adsorption from solution onto mercury electrodes will yield information regarding the latter); (b) In connection with a test of theories of the dependence of adsorption on the electric variable (this has also been carried out largely according to measurements on mercury electrodes); (c) More generally, since one may expect that the effects of HCN on processes in aqueous solution are similar to those of water (traces) on processes, both homogeneous

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and heterogeneous, in organic solutions.

BUTLER<sup>1)</sup>, when testing his theory on the role of dielectric bulk properties in the adsorption from solution (in terms of the dielectric constants,  $\epsilon$ , of the pure components in bulk), was aware of the exceptional behaviour expected for aqueous HCN solutions ( $\epsilon_{\text{HCN}} > \epsilon_{\text{H}_2\text{O}}$ ), as compared with any other aqueous solution of neutral molecules A for which  $\epsilon_A < \epsilon_{\text{H}_2\text{O}}$ , but reported that electrocapillary measurements did not confirm this expectation. Recent workers<sup>2-8)</sup> developed the theory of adsorption on electrodes from a molecular point of view, considering simultaneously double layer structure, and were again struck with the exceptional behaviour to be expected for HCN ( $\mu_{\text{HCN}} > \mu_{\text{H}_2\text{O}}$  without substantial increase in molecular size, see below). Therefore, new experiments were undertaken, involving in particular differential capacity measurements. Their results are reported here, and the controversial situation found is discussed with the aim of finding an adsorption mechanism which may explain the bulk of the observations and serve as a working hypothesis in further explorations.

## Experimental

### 1. Materials

The mercury was used as supplied from Bethlehem Apparatus Co., Hellertown, Pa. (in glass bottles from a continuous triple distillation). Hydrochloric acid was purified by distillation in the hydrogen stream, using the constant boiling fraction and diluting as necessary with conductivity water. Hydrocyanic acid was obtained as a pure solid substance (at low temperature) in an all-glass apparatus following the method described in BRAUER's HANDBUCH<sup>9)</sup>. It was melted, weighed into volumetric flasks to obtain stock solutions (which were also 0.1 N HCl) which were diluted as required with 0.1 N HCl. Hydrogen bubbling was not applied in the experiments, since it would have led to a steady decrease in HCN content of the solution. The solutions were freed from any remaining reducible species by letting mercury drop over night or at least a few hours, holding the potential of the dropping electrode at a value more than 1 V cathodic to the potential of the reversible calomel electrode in the same solution.

### 2. Techniques

Instrumentation and techniques used in the electrocapillary and differential capacity measurements have been described elsewhere<sup>10-12)</sup>.

### 3. Preliminary experiments

To test the absence of an effect on CN<sup>-</sup> on the results, preliminary experiments were carried out in solutions obtained by mixing KCN, HCl and KCl in the required amounts to make 0.1 N HCl solutions containing certain amounts of HCN. At low total salt content, the curves were nearly identical with the ones in solutions without salt but the same amount of HCN (see below). The entire branch up to calomel formation could be measured, without

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any rise in the capacity which would have indicated the presence of cyanide adsorption (*cf.* the electrocapillary experiments of ERDEY-GRÚZ and SZARVAS<sup>13)</sup> and of WROBLOWA, KOVAC and BOCKRIS<sup>14)</sup>) but with a lowering of C over a wide portion of the anodic branch of the curves. On the other hand, at high salt concentrations, larger than 1 M, HCN (about 0.1 M) had no effect on the capacity curves.

#### 4. Direct results

With the capillary electrometer, the following were determined:

- (a) With the aim of obtaining the coordinates of the electrocapillary maximum (potential,  $U^{zc}$ , at zero charge), pairs of values of potentials were found which corresponded to certain fixed values of the interfacial tension,  $\gamma$ , and an approximate value of the maximum interfacial tension was also obtained in this way. PASCHEN's method<sup>15)</sup> was then used to find  $U^{zc}$ . The values are listed in table 1.

TABLE 1. Coordinates of the point of zero charge in  
the system Hg/0.1 N HCl aq.+HCN

Concentration	$U^{zc}$ (mV vs. RCE)*	$\gamma^{zc}$ (erg cm <sup>-2</sup> )†
0	— 563	426.5
0.001 M	— 557	425.7
0.002 M	— 562	425.8
0.005 M	— 562	425.0
0.01 M	— 563	425.6
0.10 M	— 562	425.4

\* RCE denotes a reference electrode consisting of the half-cell Hg/Hg<sub>2</sub>Cl<sub>2</sub>, Cl<sup>-</sup> at the same concentration and combination as in the test solution, but without HCN.

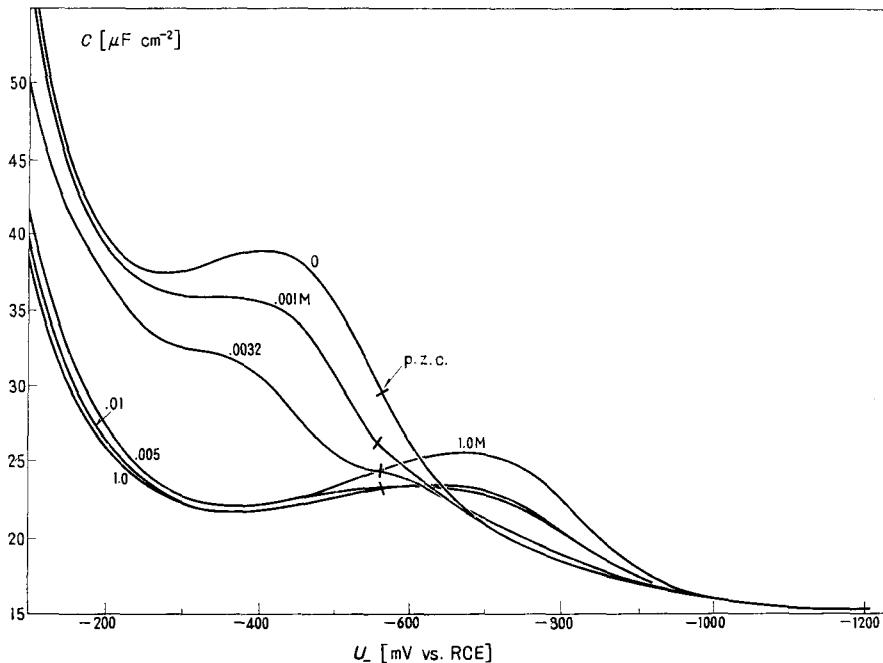
† The differences in  $\gamma^{zc}$  have been found not to be real, by measuring directly the change in interfacial tension at  $U^{zc}$  upon addition of HCN, see table 2.

- (b) With the aim of determining more accurately the absolute value of  $\gamma^{zc}$  (the interfacial tension at zero charge), its value was first set in pure 0.1 N HCl (where  $U^{zc}$  is known), and this solution was then substituted with solutions containing more and more HCN, up to 1 M, always maintaining the potential of zero charge; after every substitution, the meniscus was renewed. The results are given in table 2.
- (c) Because of the unusual results of the determinations under (a) and (b) (see below), absolute values of the interfacial tension were also measured in the same way as under (b) at several other potentials, always beginning with pure 0.1 N HCl and then substituting HCN solutions. The results

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TABLE 2. Change in interfacial tension upon addition of HCN to aqueous 0.1 N HCl (on Hg)

$U_-$ (mV vs. RCE)	$\gamma$ (erg cm <sup>-2</sup> ) in pure 0.1 N HCl	$\gamma$ (erg cm <sup>-2</sup> ) upon introduction of HCN ( $\sim 0.1$ M)
— 50	375.77	374.22
— 100	385.76	384.36
— 150	394.41	393.67
— 200	401.75	401.97
— 250	408.17	407.12
— 350	418.19	418.60
— 565	426.51	426.26



**Fig. 1.** Differential capacity curves, measured with a 2 mV peak-to-peak, 500 cps signal at a dropping mercury electrode (drop time approximately 9 sec) with aqueous solutions 0.1 N HCl + the amounts of HCN stated.

are also given in table 2.

With the impedance bridge, and using a dropping mercury electrode and solutions identical with the ones in the electrocapillary studies, differential

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capacity (C) curves were determined over the entire potential range attainable; they are shown in figure 1.

With the same electrode, the droptimes were also measured as a function of potential for some of the solutions. They were within the error limits identical with those obtained in the base solution, pure 0.1 N HCl.

### Derived results

#### 1. Adsorption of HCN from interfacial tension measurements

Within the experimental error, there was no adsorption present according to these measurements (using the capillary electrometer readings and the drop time results):

$$\Gamma_{\text{HCN}(\text{H}_2\text{O})} = -(\partial\gamma/\partial\mu_{\text{HCN}})_{\mu_{\text{HCl}}, U_-} = 0, \quad (1)$$

when the concentration of HCN was varied from 0.001 to 1 M. The condition under which this equation holds is equilibrium of the adsorbed species HCN with the species HCN dissolved in the bulk of the solution. (Here,  $\mu$  denotes chemical potential,  $U_-$  is the electrical potential of the test electrode referred to a reference electrode Hg/Hg<sub>2</sub>Cl<sub>2</sub>, 0.1 N HCl, containing no HCN.)

#### 2. Adsorption of HCN from differential capacity measurements

##### 2.1 Integration, followed by differentiation at constant potential

The differential capacity-potential data were, for each solution composition, fitted to a polynomial

$$C = a_0 + a_1 U + a_2 U^2 + a_3 U^3 + \dots \quad (2)$$

using the IBM 1620 Computer and Library Program File No. 7.0.002; the expressions obtained were integrated algebraically (taking the integration con-

TABLE 3. Surface excess of HCN at the interface Hg/0.1 N HCl aq. + HCN, as  $-(\partial\gamma/\partial\mu_{\text{HCN}})_{U_-}$  from integrated differential capacity data

$U_-$ (mV) (vs. RCE)	0.001 M	0.003 M	0.005 M	0.01 M
	$\Gamma_{\text{HCN}(\text{H}_2\text{O})}$ ( $10^{-10}$ moles cm <sup>-2</sup> )			
0	- 0.8	- 10	- 1.7	- 0.15
- 100	- 0.4	- 7.8	- 1.0	0
- 200	- 0.5	- 3.7	- 0.8	0
- 300	- 0.2	- 1.5	- 0.6	0
- 400	- 0.1	- 0.4	- 0.1	0

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stants from the invariable coordinates of the point of zero charge at all concentrations of HCN) to find the interfacial tension. (The values for 0.1 N HCl without HCN agreed within the error limits with the directly measured interfacial tensions<sup>10)</sup>). These values were then differentiated at constant potential with respect to  $RT \ln c_{\text{HCN}}$ ; this was taken as equivalent to a differentiation with respect to  $\mu_{\text{HCN}}$ , in other words any change of the activity coefficient over the concentration range was neglected. The results are given in table 3; they are affected by a rather large error since the  $\gamma - \log c$  relationship changes slope abruptly at medium concentrations; it is almost step-shaped. The results are certain as to their magnitude.

## 2.2 Use of FRUMKIN's approximations

Values of the fractional surface coverage,  $\theta = \Gamma/\Gamma_s$ , where  $\Gamma_s$  is a saturation value, were evaluated according to the relation ( $q^M$  is the charge density on the metal, subscripts refer to  $\theta=0$  and  $\theta=1$ , respectively):

$$q^M = q_0^M(1-\theta) + q_1^M\theta, \quad (3)$$

where it is assumed that covered and uncovered parts (with respect to the adsorbing solute) of the electrode behave as two capacitors in parallel<sup>16)\*</sup>. The covered part has a characteristic charge density which may be found as

$$q_1^M = C_1(U - U^{zc}) \quad (4)$$

TABLE 4. Fractional coverages  $\theta_{\text{HCN}}$  from equation 3

$U_{-}$ (mV) (vs. RCE)	0.001 M	0.003 M	0.005 M	0.01 M
	$\theta_{\text{HCN}}$			
- 50	0.21	0.41	0.68	0.73
- 100	0.18	0.40	0.78	0.82
- 150	0.22	0.45	0.89	0.92
- 200	0.25	0.51	0.93	0.96
- 250	0.28	0.54	0.96	0.98
- 300	0.32	0.61	0.97	0.98
- 350	0.37	0.67	0.97	0.98
- 400	0.42	0.73	0.95	0.97
- 450	0.48	0.80	0.94	0.95
- 500	0.55	0.88	0.92	0.94
- 600	0.37	0.42	0.68	0.68

\* ) This model will be more appropriate in the present system than in most others, cf. discussion and calculations below and Ref. 47.

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where  $C$  is assumed independent of  $U$  (and taken as the experimentally observed value of  $C$  at high coverage in the middle of the adsorption region), and  $U^{\infty}$  is the, in the present case invariable, potential of zero charge. The uncovered (or better, solvent-covered) part of the electrode has a characteristic charge density  $q^{\infty}$  which may be taken as that of the system in absence of adsorption. Values of  $\theta$  obtained with the assumption  $C_1=22 \mu\text{F cm}^{-2}$  (*cf.* figure 1, anodic branches) are shown in table 4.

To a further approximation, also due to FRUMKIN (*cf.* Ref. 16, page 181), values of  $\theta$  were evaluated according to the relation (subscripts as in equ. (3))

$$C = C_0(1-\theta) + C_1\theta, \quad (5)$$

where  $C_0$  was taken from the experimental capacity curve in pure 0.1 N HCl. The results of this are shown in table 5. Fig. 1 indicates that  $\theta_{\text{HCN}}$  approaches 0 rapidly at potentials more negative than  $-600$  mV.

TABLE 5. Fractional coverages  $\theta_{\text{HCN}}$  from equation 5

$U_-$ (mV) (vs. RCE)	0.001 M	0.003 M	0.005 M	0.01 M
	$\theta_{\text{HCN}}$			
- 50	0.04	0.13	0.41	0.50
- 100	0.02	0.23	0.46	0.49
- 150	0.02	0.15	0.55	0.60
- 200	0.03	0.14	0.69	0.76
- 250	0.03	0.23	0.85	0.89
- 300	0.11	0.33	0.95	0.98
- 350	0.15	0.39	1.00	1.01
- 400	0.23	0.49	0.99	1.01
- 450	0.26	0.64	0.97	0.99
- 500	0.36	0.75	0.93	0.95
- 550	0.50		0.85	0.85
- 600	0.46	0.57	0.65	0.63

## 2.3 Integration, followed by differentiation at constant charge

From a thermodynamic point of view, one should expect<sup>10,17-19</sup>

$$(\partial\gamma/\partial\mu_A)_{\mu_{\bar{A}}\neq_1,A,v} = (\partial\gamma/\partial\mu_A)_{\mu_{\bar{A}}\neq_1,A,qM} - q^M(\partial\Gamma_{A(1)}/\partial q^M)_\mu, \quad (6)$$

both sides of equation (6) being equal to the negative of the relative surface excess of A. It turned out that in the case where A=HCl (or its ionic components) in dilute solutions<sup>10</sup>, this equation was not satisfied when  $\gamma$  was

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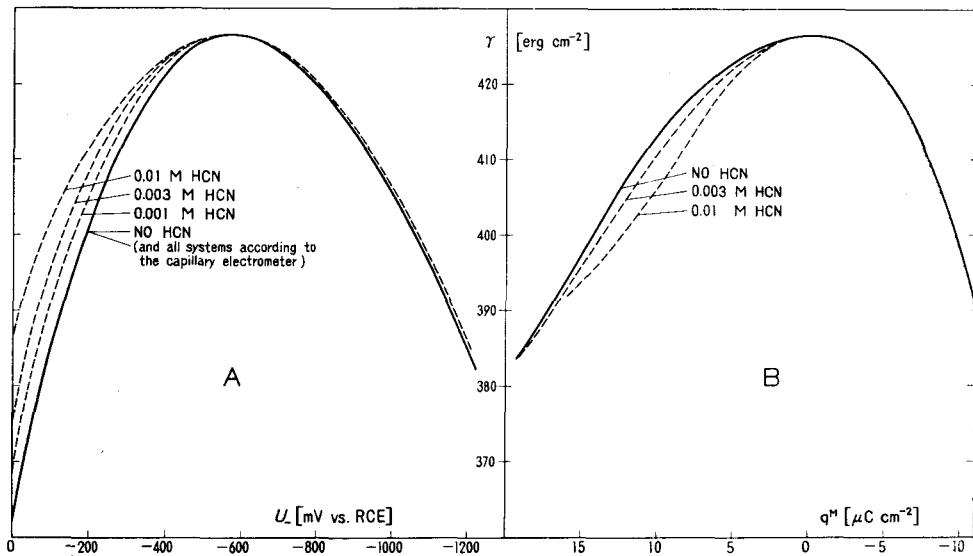
obtained by integration from the differential capacity data (let this be denoted with  $\gamma_c$ ). The right-hand side gave apparently the correct results whereas those of the left-hand side deviated increasingly from results obtained using direct electrocapillary data (let these latter be denoted  $\gamma_m$ ). As an expression of the same situation, plots of  $\gamma_c$  and  $\gamma_m$  against  $U$  were discordant, but those of  $\gamma_c$  and  $\gamma_m$  against  $q^M$  were in accord.

In figure 2,  $\gamma_c$  and  $\gamma_m$  are plotted for the present case agains  $U$ . (part A) and against  $q^M$  (part B). Clearly, the values of  $(\partial\gamma/\partial\mu_{HCN})_{\mu_i \neq H_2O, HCN, qM}$  are negative; hence there must be a positive surface excess at least where  $\partial\Gamma_{HCN(H_2O)}/\partial q^M = 0$ . According to the results of the approximate methods (subsection 2.2 above), this is true for  $q^M \approx 5 \mu C \text{ cm}^{-2}$ . (It is, incidentally, for this point of maximum adsorption that the approximations hold best). With this initial condition, values of  $\Gamma_{HCN(H_2O)}$  were evaluated by the pointwise procedure described before<sup>10</sup>. The evaluation could not be begun at  $q^M=0$ , in the present

TABLE 6. Surface excess of HCN at the interface Hg/0.1 N HCl  
aq.+HCN, as  $-(\partial\gamma/\partial\mu_{HCN})_{qM} - q^M(\partial\Gamma_{HCN(H_2O)}/\partial q^M)_{\mu_{HCN}}$ ,  
from integrated differential capacity data

$q^M (\mu C \text{ cm}^{-2})$	0.001 M	0.003 M	0.005 M	0.01 M
	$\Gamma_{HCN(H_2O)} (10^{-10} \text{ moles cm}^{-2})$			
0	0.04	0.02	0.00	0.00
1	0.05	0.32	0.23	0.01
2	0.04	0.58	0.40	0.01
3	0.04	0.74	0.51	0.02
4	0.05	0.85	0.56	0.02
5	0.05	0.85	0.56	0.02
6	0.05	0.85	0.56	0.02
7	0.05	0.78	0.51	0.01
8	0.04	0.64	0.47	0.01
9	0.03	0.46	0.44	0.00
10	0.03	0.24	0.38	- 0.01
11	0.02	0.00	0.35	- 0.01
12	0.02	- 0.23	0.31	- 0.01
13	0.01	- 0.44	0.24	- 0.01
14	0.01	- 0.61	0.17	- 0.01
15	0.00	- 0.73	0.07	- 0.02
16	- 0.01	- 0.84	- 0.02	- 0.02

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**Fig. 2.** Electrocapillary curves for the system Hg/0.1 N HCl aq. + HCN (concentrations stated in the figure; solid lines: pure 0.1 N HCl). Values calculated from the capacity data reported in figure 1 by integration using constants derived from tables 1 and 2. Part A: Plot against the potential as measured against the half-cell Hg/Hg<sub>2</sub>Cl<sub>2</sub>, 0.1 N HCl (without HCN) Part B: Plot against the charge density on the metal.

case, since  $(\partial \Gamma_{\text{HCN}(\text{H}_2\text{O})}/\partial q^M)_\mu$  is not constant around this point, and therefore,  $q^M(\partial \Gamma_{\text{HCN}(\text{H}_2\text{O})}/\partial q^M)_\mu = (\partial \Gamma_{\text{HCN}(\text{H}_2\text{O})}/\partial \ln q^M)_\mu$  is indefinite around  $q^M=0$ . The values obtained with the equivalent condition  $(\partial \Gamma_{\text{HCN}(\text{H}_2\text{O})}/\partial q^M)_\mu=0$  at  $q^M=5 \mu\text{C cm}^{-2}$  are given in table 6.

## Discussion

### 1. Physical significance of the results

#### 1.1 Negative values of the surface excess

Such values of the adsorption of HCN are reported in table 3. They appear impossible if they are considered as true surface excesses, an approximation usually considered to be very satisfactory in dilute solutions:<sup>\*)</sup> A

<sup>\*)</sup> By definition

$$\Gamma_{\text{HCN}(\text{H}_2\text{O})} \equiv \Gamma_{\text{HCN}} - \frac{x_{\text{HCN}}}{x_{\text{H}_2\text{O}}} \Gamma_{\text{H}_2\text{O}} = -(\partial \gamma / \partial \mu_{\text{HCN}})_{\mu_i \neq \text{H}_2\text{O}, \text{HCN}, \nu} \quad (7)$$

where  $\Gamma_{\text{HCN}(\text{H}_2\text{O})}$  is the relative surface excess which is determinable,  $\Gamma_{\text{HCN}}$  and  $\Gamma_{\text{H}_2\text{O}}$  are true surface excesses, and  $x$  are mole fractions. With the results of table 3, if  $\Gamma_{\text{HCN}}$  was to have positive values,  $\Gamma_{\text{H}_2\text{O}}$  would have to assume extraordinarily large positive values, in view of the small value of  $x_{\text{HCN}}/x_{\text{H}_2\text{O}}$ .

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negative surface excess of  $1 \cdot 10^{-10}$  moles  $\text{cm}^{-2}$  at a concentration of  $3.2 \cdot 10^{-6}$  moles  $\text{cm}^{-3}$  would mean approximately the expulsion of HCN from a solution layer at the electrode of 3000 Å thickness! In addition, the negative surface excesses, if meaningful, should not reach any limiting value with increase in concentration, and in particular, this limiting value could not be zero, as indicated in table 3. (*Cf.* in this connection the negative surface excesses of salts at the solution-air interface quoted by HARKINS<sup>20)</sup>).

### 1.2 Zero adsorption

Several improbable assumptions are necessary to understand physically the results of table 2: For example, the interfaces Hg/HCN and Hg/ $\text{H}_2\text{O}$  might have the same interfacial tension *at all potentials*; the free energies of adsorption of HCN and  $\text{H}_2\text{O}$  might be equal, and therefore the interface might have the same composition as the bulk phase. Unfortunately, neither of these quantities appears to be known for the interface Hg/HCN\*); at any rate, such assumptions are highly improbable (see below).

The data of BLOMGREN, BOCKRIS and JESCH<sup>21)</sup> suggest a very small difference in the free energies of adsorption, and hence very little adsorption, for aliphatic substances completely soluble in water (in fact, the adsorption of methanol from water<sup>22)</sup> and the adsorption of butanol from methanol<sup>23)</sup> are not very great). However, even if zero adsorption of HCN from  $\text{H}_2\text{O}$  can be understood on this basis at the point of *zero charge*, then it remains unclear why the highly polar molecules of HCN should not be attracted to the *electrified* interface (see below).

### 1.3 The isotherms in the cases of non-zero adsorption

The results of tables 4 and 5 indicate zero adsorption near the potential of zero charge and at negative surface charges. At positive charges (with a maximum at  $q^M = 5 \mu\text{C cm}^{-2}$ ), adsorption appears to follow an ordinary type of isotherm, for example some type of LANGMUIR isotherm; a saturation value is reached at high concentrations near the charge density of maximum adsorption. This is the behaviour observed commonly for the adsorption of neutral substances on electrodes.

The results of table 6 indicate zero adsorption near the point of zero charge and at negative surface charges. At positive charges, adsorption appears to follow an unusual type of isotherm: Zero adsorption at low *and high* concentrations, a maximum of adsorption at medium concentrations for each

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\*) With the present experimental setup, greater concentrations of HCN in aqueous solution or pure HCN could not be handled without danger of poisoning people

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given charge density. This is difficult to understand on the basis of a mixed isotherm (competitive adsorption of solvent and solute).

## 2. Predictions of BUTLER's theory

BUTLER<sup>1)</sup> described the potential dependence of the adsorption of neutral molecules from solution in terms of their dipole moment and polarisability (expressing the latter through the *bulk* dielectric constant,  $\epsilon$ ), as compared to those of the solvent. Accordingly, HCN ought to become increasingly adsorbed, at constant solution composition, when going to potentials further away from the point of zero charge. Butler himself noted, without stating details, that electrocapillary measurements did not reveal such an effect. However, there is a new version of this theory by DEVANATHAN and TILAK<sup>24)</sup> which relates the polarisability more correctly to molecular dimensions and values of the dielectric constant appropriate for the electric double layer. It appears that this yields qualitatively the same prediction, as long as  $A_{\text{HCN}}/\epsilon_{\text{HCN}}^{\text{dl}} < A_{\text{H}_2\text{O}}/\epsilon_{\text{H}_2\text{O}}^{\text{dl}}$  ( $A$ =molecular area at the interface,  $\epsilon^{\text{dl}}$  a double layer dielectric constant).

## 3. Predictions of FRUMKIN's theory

FRUMKIN<sup>25-27)</sup> described the potential dependence of the adsorption of neutral molecules from solution in terms of a capacitor-in-parallel model of the covered and uncovered parts of the electrode surface. In this theory, the specific values of the capacities at full and zero coverage and an additional isotherm parameter which accounts summarily for lateral interactions, are taken from the experimental capacitance curves<sup>16)</sup>, in most applications. However, the work terms in FRUMKIN's theory (due to the capacity and potential changes upon adsorption) can be related<sup>16)</sup> to the ones in BUTLER's theory (due to the changes in polarisability and dipole moment), and results similar to those quoted above should be obtained when predicting the adsorption of HCN from aqueous solution.

The experimental data have been evaluated only with an approximate form of FRUMKIN's theory (see above). An exact analysis cannot be applied because, obviously, the shift of the potential of zero charge upon adsorption of a monolayer of HCN could not be determined from the experimental data nor could any interaction parameters be inferred from the shape of adsorption-desorption peaks<sup>16)</sup> since none are present.

## 4. Predictions of the theory of BOCKRI *et al.*

A theory of the charge dependence of adsorption of neutral molecules on electrodes was developed by BOCKRIS and coworkers<sup>2-8)</sup>. It is particularly suited

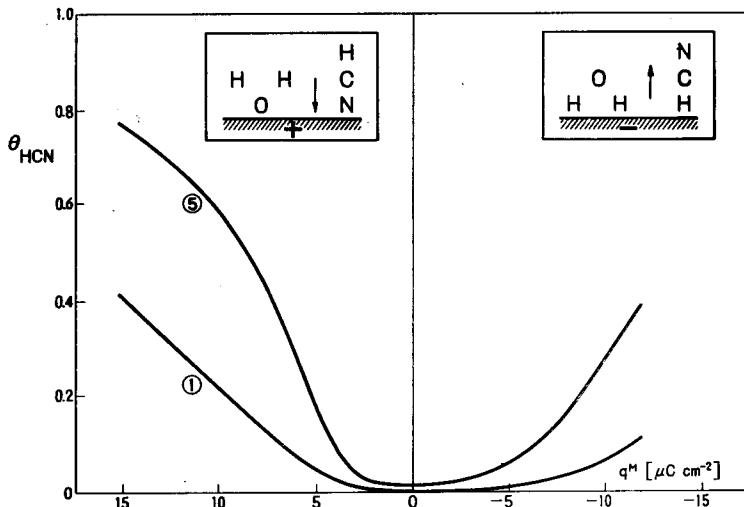
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for predictions of the type desired here since the calculations are based on a molecular model of the interface. This theory was tested with several substances (butanol, phenol, benzene) as solutes adsorbed at the interface Hg/aqueous solutions. These are all desorbed at increasing charge density, owing to the more effective field-solvent dipole interaction. For the present system Hg/H<sub>2</sub>O (0.1 N HCl) + HCN, it is developed from the general equations<sup>23)</sup> as follows, assuming H<sub>2</sub>O-HCN competition in a varying field in which both dipolar species are fully immersed.

- (i) The electric part of the free energy of adsorption of water,  $\langle \Delta G_{H_2O}^e \rangle$  (as an average per molecule) can be calculated as before<sup>2,23)</sup>, rewriting the equations

$$\langle \Delta G_{H_2O}^e \rangle = B_{H_2O} \left( B_{H_2O} E_{H_2O} + \mu_{H_2O} F + \frac{1}{2} \Delta \Delta G_{H_2O}^e \right) \quad (8)$$

where  $B = (N_\uparrow - N_\downarrow)/N_T$ , an expression for the net orientation of water molecules at the interface,  $N$ =number,  $\uparrow$  and  $\downarrow$  refer to the dipole orientation as shown in the insert, figure 3, T designates total,  $E$  is the lateral



**Fig. 3.** Fractional coverage of the electrode by HCN as calculated by theory (equations 8-10), using  $|E_{H_2O}/RT| = 2$ ,  $\Delta \Delta G_{H_2O}^e/RT = 1$ ,  $\Delta \Delta G_{HCN}^e/RT = 2$ ,  $\mu_{H_2O} = 1.84$  D,  $\mu_{HCN} = 2.95$  D,  $F = 4\pi q^M/\epsilon$ ,  $\epsilon = 6$ . Circled values given in the figure are relative values of  $(\theta_{HCN}/\theta_{H_2O}) \exp(-\Delta G_{HCN}^e/RT)$ . Inserts show the positions taken up by the molecules of water and hydrocyanic acid upon (extreme) charging of the electrode with the sign indicated.

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dipole-dipole interaction energy per molecule,  $\mu$  the dipole moment,  $F = 4\pi q''/\epsilon$  is the double layer field,  $q''$ =charge density on the metal,  $\epsilon$ =dielectric constant, taken as six<sup>11)</sup>, and  $\Delta\Delta G_{H_2O}^e \equiv \Delta G_r^e - \Delta G_i^e$  is an energy term expressing the difference in the non-fielddependent energies of attachment of H<sub>2</sub>O in the two positions.

- (ii) The electric part of the free energy of adsorption of HCN,  $\langle \Delta G_{HCN}^e \rangle$  (as an average per molecule) is calculated from the general equations given before which may be rewritten for the present case in a simpler way as

$$\langle \Delta G_{HCN}^e \rangle = B_{HCN} \left( \mu_{HCN} F + \frac{1}{2} \Delta\Delta G_{HCN}^e \right) \quad (9)$$

where  $B$ ,  $\mu$ ,  $F$  and  $\Delta\Delta G^e$  have the same meanings as above, and where it is assumed, (a) that there are no lateral interactions between the HCN dipoles, (b) that the HCN dipoles are fully immersed in the inner part of the double layer, as are those of water, (c) that the same dielectric constant\* is appropriate for HCN as is for water when calculating the dipole-field interaction, *i.e.*  $F = 4\pi q''/\epsilon$ ,  $\mu = 2.95$  D and hence  $\mu_{HCN}F/kT = 0.45 q''$  (if  $q''$  is expressed in  $\mu\text{C cm}^{-2}$ ), (d) that the HCN dipoles are in an orientation normal to the interface, as are those of water. The difference,  $\Delta\Delta G_{HCN}^e$ , in the strength of attachment of the HCN dipoles to the metal (either with N or with H toward the electrode) was taken as  $2 RT$  in favour of the anodic orientation (N toward the electrode); this is twice the value taken for water, and is chosen somewhat arbitrarily since it does not affect the result significantly.

- (iii) The coverage,  $\theta$ , of the interface by HCN was calculated, as before for other species, by an equation which simplifies in the present case to

$$\theta/(1-\theta) = (c_{HCN}/c_{H_2O}) \exp(-\Delta G_{HCN}^{ads}) \exp(\langle \Delta G_{H_2O}^e \rangle - \langle \Delta G_{HCN}^e \rangle), \quad (10)$$

assuming that HCN replaces water molecules on a stoichiometric basis 1 : 1 from the interface, and treating (in the actual calculations) the activity ratio  $c_{HCN}/c_{H_2O}$  and the exponential of the free energy of adsorption,  $\Delta G_{HCN}^{ads}$ , as a parameter.  $\Delta G_{HCN}^{ads}$  is the hypothetical free energy of replacement of a monolayer of H<sub>2</sub>O by one of HCN at zero charge and with  $B=0$  for

\* ) Note that "the same dielectric constant" refers to the constant appropriate to calculate the field strength in the compact part of the double layer, which is essentially monomolecular. It does *not* include that part of the permittivity due to orientation polarisation which arises as a consequence of the reorientation of the adsorbed molecules by the field. The latter is small as compared to the value of the dielectric constant under consideration, but it is of prime importance for the work of adsorption of polar molecules.

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both species which, if data from vapour phase measurements are available, may be calculated using a cycle which includes evaporation from solution. —The results of the present calculation are shown in figure 3.

It is noted that the curves have a minimum around the point of zero charge, rather than the usually observed maximum; they have no maximum. If repulsion between adsorbed HCN molecules (with their dipoles parallel) had been taken into account (which, in comparison with water interactions, would be a significant term only at coverages of 30% and more\*\*), the effect would have been to make the ascents toward saturation coverage less steep.

An adsorption behaviour such as shown in figure 3 has not been verified quantitatively so far. However, it has been verified qualitatively for the adsorption of water from organic solvents, first by FRUMKIN<sup>28,29</sup>, later by PARSONS and DEVANATHAN<sup>22</sup> and by KIRKOV<sup>30</sup>, who found the adsorption of water to vary with field strength in the manner indicated by the curves of figure 3.

##### 5. Predictions of FOWKES' theory

The absolute value of the interfacial tension Hg/HCN can be calculated, according to FOWKES<sup>31,32</sup>, as

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^d \gamma_2^d)^{1/2} \quad (11)$$

where 1 and 2 refer to Hg and HCN, respectively, and superscript d denotes the part due to dispersion forces. For  $\gamma_{\text{Hg}}^d$ , FOWKES established a value of 200 erg cm<sup>-2</sup> in calculations involving water, hydrocarbons and mercury. For  $\gamma_{\text{HCN}}^d$ , it may be appropriate to take the full value of  $\gamma_{\text{HCN}} = 18$  erg cm<sup>-2</sup><sup>33</sup>) since at 25 °C, the liquid is near the boiling point; dipole-dipole forces (as in the case of HCl, which has a similarly narrow range of liquid state) may account for less than 20% of  $\gamma_{\text{HCN}}$ <sup>34</sup>.

Equation (11) gives a value for the interfacial tension of 382 erg cm<sup>-2</sup>. This is considerably lower than the interfacial tension of the Hg/H<sub>2</sub>O interface and would, by itself, constitute an argument for adsorption of HCN. The possibility of spreading of HCN at the mercury-water interface may be estimated from another equation of FOWKES<sup>31</sup>,

$$\gamma_{13} - (\gamma_{23} + \gamma_{12}) = 2[(\gamma_2^d \gamma_3^d)^{1/2} + (\gamma_2^d \gamma_1^d)^{1/2} - (\gamma_1^d \gamma_3^d)^{1/2} - \gamma_2] \quad (12)$$

where 3 refers to water. Using  $\gamma_3^d = 21.8$  erg cm<sup>-2</sup>, as suggested by FOWKES, one obtains (for the right-hand side) a small negative value, hence HCN should

\*\*) With molecules such as butanol adsorbed from water, a significant interaction, as compared to that between water dipoles, should arise only at coverages of upward 80% since the dipoles, though strong, are in a part of the double layer where the dielectric constant is much higher than that in the inner part relevant here.

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not spread. Of course, this result must be taken with caution, not so much because of the approximate nature of the numerical values but because of the solubility of HCN in  $H_2O$ , and also because this calculation refers to the *charge-free* interface only. Moreover, the right-hand side of equation (12) gives a *large* negative value in the case of spreading of water at the mercury-butanol interface, which is contrary to observation<sup>30)</sup> at non-zero charge. It may, therefore, be concluded that the adsorption of HCN at zero charge is improbable but becomes *probable* as the interface is electrified; the probability is greater than in the case of  $H_2O$  adsorbed from butanol, by equation (12).

#### 6. Related experimental observations

BOCKRIS and CONWAY<sup>35)</sup> observed the poisoning effect of HCN in 0.1 N HCl on the hydrogen evolution reaction on nickel, starting at a concentration of  $10^{-10}$  M, which should correspond to a very small coverage (note also that these results refer to negative surface charges of the nickel electrode), but very high poisoning activity. Other direct observations on the adsorption of HCN from solution seem to lack in the literature. WEISSMANTEL<sup>36)</sup> observed the chemisorption of HCN from the gas phase on Pt (clean or previously covered with oxygen), and these measurements indicate a strong metal-HCN interaction. DUNKEN and HOBERT<sup>37)</sup> observed dissociative adsorption of HCN on Rh, Pd, and Ag. Other direct evidence seems to be given only in the well-known poisoning of catalysts which has, because of the small amounts necessary, usually been explained with the active centre theory. These observations, though sparse, suggest that some adsorption of HCN is possible.

#### 7. Suggestions regarding the model of adsorption of HCN

The most probable conclusion regarding the adsorption of HCN on the basis of the foregoing discussion and the present experimental material is: There is zero adsorption of HCN on the cathodic side and at zero charge on the metal, but there is positive adsorption at positive surface charges. The thermodynamic evaluation procedures appear to be invalidated in the sense that, (a) the electrocapillary measurements do not indicate any adsorption, probably because there is no equilibrium between the species HCN found in solution and that at the interface, (b) the capacity measurements indicate adsorption; their evaluation gives contradicting results for the same reason as given in (a), but, since the capacity is a direct measure of the redistribution of charges and dielectric material at the interface, it may be taken as the starting point for a model of the interface in the presence of HCN.

The capacity curves (figure 1) are affected in their anodic portion (and a little around the potential of zero charge). The well-known hump, clearly

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visible in the curve for pure 0.1 N HCl, disappears gradually as HCN is added until a flat minimum is observed in its place. This minimum resembles closely that on the cathodic side and it is separated from it, at sufficiently high HCN concentrations, by a flat maximum; the curves are almost symmetric then.

In order to understand the significance of this, one should recall how the hump and the cathodic minimum (as features of the capacity curve in nearly all aqueous solutions) have been explained. DEVANATHAN<sup>38)</sup> has suggested that there is contact adsorption\*, neither of anions nor of cations, at the unique cathodic minimum (this is almost independent of cationic or anionic species present). BOCKRIS, DEVANATHAN and MÜLLER<sup>2)</sup> have explained this constancy of the capacity value, assuming again that no ions are in direct contact with the electrode, and further that they are present as *hydrated* ions adjacent to a *hydrated* electrode. In the same paper, the anodic hump of the capacity-potential (or -charge) relation was explained by the particular properties of the adsorption isotherms of anions in contact with the electrode, and this was further developed and in great part quantitatively verified by WROBLOWA, KOVAC and BOCKRIS<sup>14)</sup>.

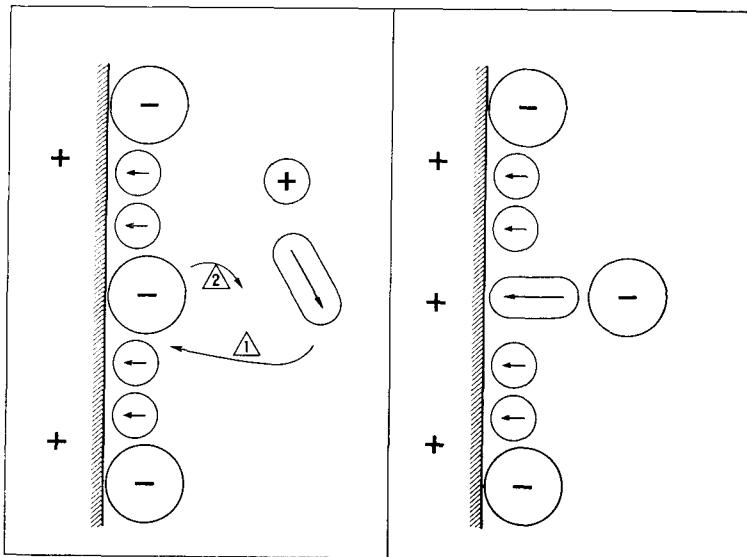
From these aspects of double layer theory, a consistent explanation of the shape of capacity-potential curves in presence of HCN arises as follows: As the concentration of HCN increases at a given HCl concentration, there is a tendency toward preferential solvation of the ions by the HCN dipoles. In particular, HCN molecules will move where the field is strongest, namely near the (unhydrated<sup>2)</sup>) anions ( $\text{Cl}^-$ ) in contact with the electrode. In this process, they will displace these ions outward, and in principle more strongly at positive electrode charges which allow an energetically favourable attachment of the HCN molecules (with the nitrogen end, which has a lone electron pair) to the electrode. These anions will now be at the outer Helmholtz plane, and the capacity should be lowered as observed.

It seems that the  $\Gamma$  values evaluated from the capacity data under the "constant charge" condition may thus not be taken as a measure of the adsorption of HCN but rather as a measure of the rate of entry\*\* of HCN in the double layer. The capacity values ought to reflect the process of exchange of a  $\text{Cl}^-$  ion in contact with the electrode by one which is separated from the

\*) Contact (or specific) adsorption is a term for the state of adsorbate molecules or ions in immediate contact with adsorbent molecules. Ions not so adsorbed form the well-studied diffuse part of the "double" layer; adsorbed neutral molecules not in contact with the adsorbent are far less studied.

\*\*) That is, a measure of  $\partial \Delta \Gamma_{\text{HCN}(\text{H}_2\text{O})} / \partial U$  where the potential,  $U$  is a periodic function of time;  $\Gamma_{\text{HCN}(\text{H}_2\text{O})}$ , the surface excess of HCN in the particular position proposed, attains a limiting value (see below) at high HCN concentration, and so does  $C$ .

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**Fig. 4.** The mechanism suggested for the adsorption of HCN at a positively charged interface; the metal-solution interface is shown before adsorption of HCN (or in the cathodic half-cycle of the signal in the a.c. measurements; left-hand side) and after adsorption of HCN (or in the anodic half-cycle of the signal; right-hand side).  $\triangle$  and  $\triangle$  indicate two steps of the adsorption process; circles with arrow: water molecules; circles with minus sign: anions; elongated figure with arrow: an HCN dipole.

electrode by an HCN dipole. Such a process was first indicated by BOCKRIS *et al.*<sup>10)</sup> (mechanism III of their figure 7) and is in a more complete manner shown in figure 4. It is suggested that the present observations constitute another example for the detection by differential capacity measurements of double layer processes which remain unnoticed in the stationary electrocapillary measurements.

From the viewpoint of solvation, there is evidence that this may occur preferentially by HCN, by analogy to the work of BOCKRIS and EGAN<sup>39)</sup> who explained salting-out effects in organic/aqueous solvents which were contrary to the dielectric continuum theory of salting-out effects, by preferential hydration of ions in the mixed solvent; and more directly in the results of GOPAL and HUSSAIN<sup>40)</sup> who suggest a proton donor type attachment of HCN molecules to anions and strong dipole-charge interaction in their attachment to cations (here, analogously, the positive electrode). KIRKOV<sup>30)</sup> proposed a similar attachment of water to  $\text{Li}^+$  ions at the interface mercury/butanol

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solutions containing a little water.

Within the present work, this mode of adsorption is consistent with the maximum value of  $\Gamma_{\text{HCN}(\text{H}_2\text{O})}$  observed which corresponds to a 1 : 1 ratio of adsorbed HCN molecules and  $\text{Cl}^-$  ions which may be in contact with the electrode at this charge density and concentration<sup>14)</sup>. If it is suggested that this type of interfacial complex is very stable, then this may also explain the apparent absence of correspondence with the bulk activity (failure of the electrocapillary method to detect adsorption). The decrease of surface activity of HCN at higher ionic strengths supports the assumed importance of ionic solvation by HCN (see Section on preliminary experiments). The suggested mode of adsorption explains further the activity of HCN as a catalyst poison<sup>35)</sup>: even at small coverages, it may effectively block the discharge step by its attachment in the path of charge transfer, namely, if the critical system is considered as a polar structure similar to the adsorbed [ion-ion image] or [ion-counter charge on the electrode] complex as discussed above. (In the case of Ni in alkaline solution, the observed poisoning effect is noted, already at  $10^{-10}$  M HCN, but does not increase much with HCN concentration. It rather seems to drop off at concentrations above 0.1 M. This appears to be consistent with the operation of the catalytic mechanism, where only the preceding discharge step is inhibited as described.)

The model of catalyst poisoning by HCN proposed here does not require the presence of active centres. It only requires that a sufficient amount of HCN is adsorbed from solution to become interspersed at the sites of charge transfer which are present at any given time. At a coverage of the electrode by HCN of only 1%, the maximum distance between a given adsorbed HCN molecule and a free lattice site adjacent to the solution is about 20 Å, a distance travelled rapidly under the action of strong field gradients by the highly polar HCN molecule. The actual poisoning action can be quantitatively estimated only if the complex decay constant of the critical system-HCN complex were known; maximum poisoning action may be expected if the complex decay constant (per  $\text{cm}^{-2}$ ) is of the same order of magnitude as the rate constant for the forward reaction of the critical system. At a coverage of 1% and with a complex decay of  $1 \text{ sec}^{-1}$ , a rate of discharge of approximately  $1 \mu\text{A cm}^{-2}$  should be significantly inhibited. The crystal plane model of catalysts<sup>41,42)</sup> is thus a rather satisfactory model in the present context.

The experimental results on the capacity in the present system should be more extensively analysed. For this, however, they should be given for a range of concentrations and species of *electrolytes* (and possibly solvents) with which the model of adsorption of HCN would have to be tested. On the theoretical

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side, it appears that the adsorption of HCN from  $\text{H}_2\text{O}$  cannot be explained satisfactorily by a direct solvent-solute competition, since the attachment suggested involves a competition with ions. As the electrode is more highly positively charged, the energy of the ions in the field increases more quickly than that of the HCN dipoles. Therefore, HCN may only be adsorbed at medium charges but is desorbed at extreme charges. (According to solute-solvent competition theory, the adsorption of HCN would continue to rise with  $|q^M|$ .)

#### **8. Consequences for the development of molecular theories of adsorption**

In general, a neutral solute, A, may be expected to compete for adsorption sites with all other components of the solution. From double layer work, it is known that among the simple ions, J, only the anions are adsorbed appreciably in contact with the electrode. If the adsorption of A from a solution in the solvent S, also containing J, is studied, then it must without approximation be considered as a competition between A and S and between A and J. The theory proposed by BOCKRIS *et al.* (as well as all others) is based on the approximation of competition between A and S only, and it was tested with substances A which, as far as the inner part of the electric double layer is concerned, are less polar than the solvent. It may be expected, in this case, that the extent of ionic contact adsorption affects adsorption from aqueous solution only quite indirectly, in terms of a correction (proportional to  $\theta_J^{23)}$  and the hydratability of J<sup>2,43)</sup>) to the A/S competition, in view of the preferential solvation of ions by the more polar component of the solution<sup>39,40)</sup>. However, in the case where the neutral solute A is more polar than the solvent, A/J competition becomes important. Of course, the adsorption of J depends in turn on the competition with S<sup>44)</sup>. In absence of further developments of the theory in this direction, it may be best to relate adsorption data directly to the measured capacity as in FRUMKIN's approximations, although this has the serious restriction that no absolute values can be obtained; or, if it can be substantiated that the values in table 6 have differential character (see Footnote p. 128), by integrating them with respect to chemical potential.

#### **9. Future work on the system**

The present work indicates in which direction the problem should be further attacked.

- (a) Studies (electrocapillary and capacity) at high HCN concentrations, including pure HCN and HCN containing traces of water.
- (b) Studies of the components of charge, analogous to that in the work of

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CONWAY, BARRADAS, HAMILTON and PARRY<sup>45)</sup>, for solutions containing HCN and electrolytes having different cations and anions and a range of concentrations.

These studies were outside the scope of the measurements when the present work was carried out<sup>46)</sup>, and in part the experimental setup was inappropriate (the handling of liquid HCN requires extensive safety measures).

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*Note added in proof.* Gilman<sup>48)</sup> has found that carbon monoxide displaces chloride ions from a platinum electrode. This is just the same situation as that found in the present work with HCN. The free CO molecule does not have an appreciable dipole moment. Induced polarity (due to the bonding to the metal surface, as discussed by Gilman) may have the same effect as the high permanent moment of HCN in absence of adsorption 'activated' by bonding. It remains to be seen whether the ions are completely removed from the double layer or only displaced as shown in figure 4 above. Gilman's dynamic method will reveal only ions in contact with the electrode.

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