48. *Adsorption of Gold from Cyanide Solutions by Anionic Resins.*

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Adsorption of anions on both strong- and weak-base ion-exchange resins is a function of the charge on the anion, its polarisability as measured by ionic refractivity and, less, of its shape and chemical nature. The swollen volume of a resin in a given salt form depends upon similar factors. The high affinity of Amberlite I.R.A. 400 for complex cyanides in general is due to their high polarisability. With multivalent anions adsorption is limited by the increased distance between the ionised resin sites and the equilibrium position of the adsorbed anion at the " centre of gravity " of these groups which reduces the polarisation of these anions by the resin cation groups. This effect becomes most important with weak-base resins in alkaline solution, the distance between the resin sites and the multivalent anions becoming large relative to the ionic radii of the latter owing to the low degree of ionisation of the resin. The multivalent anions are then displaced by highly polarisable singly charged ions, such as aurocyanide, as singly charged ions can take up the same position relative to the ionised resin sites irrespective of the spacing of the functional groups in the resin matrix. It has been calculated that the selectivity coefficients for aurocyanide's displacing a multivalent anion should decrease logarithmically with the four-third root of the capacity on a volume basis if the cross-linking of the resin remains constant; this relation holds in practice.

Gold, as aurocyanide ion, is strongly adsorbed[1] by the strong-base resin Amberlite I.R.A. 400 from alkaline cyanide solutions. Base-metal complex cyanides are also strongly adsorbed by this resin and, as these predominate in actual cyanide liquors, they must be selectively eluted before the gold if the resin is to be used for gold recovery. Aurocyanide can be selectively adsorbed [2] (by weak-base resins) from cyanide liquors containing excess of base-metal cyanides, thus making such preliminary elution unnecessary. Complete elution of the gold was somewhat difficult from both strong- and weak-base resins, but was satisfactory when organic solvent–mineral acid mixtures or aqueous solutions containing thiocyanate or perchlorate ions were used. The introduction of *ca.* 8—10% of strong-base groups, out of the total active groups present, increased the weight of gold adsorbed from a given solution by a weak-base resin, although this was at the expense of some selectivity of the resin for gold.

We have tried to interpret these results theoretically and, in particular, to explain the much greater selectivity of weak-base resins for aurocyanide over the base-metal cyanides than that of strong-base resins. We have tried to generalise the results for application to all anion-exchange systems.

EXPERIMENTAL

Equilibria with Amberlite I.R.A. 400 (40/60 mesh, capacity 3·74 mequiv./g. of dry chloride form) were measured by using ^{198}Au as tracer, this being prepared by neutron bombardment of ^{107}AuCN in the Harwell pile, followed by dissolution of the product in the calculated quantity of potassium cyanide solution. The resulting solution had pH 7 and contained no excess of cyanide ions. Solutions containing potassium aurocyanide of known specific activity, together with a known concentration of the sodium salt of the exchangeable ion A^- being studied, and sufficient resin in the A^- form to adsorb a large proportion of the aurocyanide, were contained in a 250 ml. beaker fitted with a magnetic stirrer and the solution was circulated continuously through a flow counter tube connected to a count ratemeter and pen recorder by means of a " Sigma " pump. Resin was kept out of the counter tube by a sintered-glass disc on the end of

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[1] Burstall, Forrest, Kember, and Wells, *Ind. Eng. Chem.*, 1953, **45**, 1648.

[2] Aveston, Everest, Kember, and Wells, *J. Appl. Chem.*, 1957, in the press.

the pump intake tube. The natural activity of the potassium associated with the aurocyanide was always an insignificant fraction of the total activity. From the activity of the solution at resin–solution equilibrium (after 1—2 hr.) and the activity of the original aurocyanide solution added (after application of decay and dead-time and background corrections), the amount of gold in solution at equilibrium, and hence the amount of gold adsorbed by the resin and the amount of A^- liberated from the resin, were calculated. Sufficient data were thus available to calculate K_A^{Au} (the equilibrium constant for aurocyanide displacing the ion A^- from the resin) at that particular gold loading. Repetition of this procedure by addition of further aliquot portions of aurocyanide to the same solution gave further values of K_A^{Au} at higher gold loadings. A complete curve of K_A^{Au} at various gold loadings on the resin was thus obtained.

The pure weak-base resin J.A.1 was prepared from chloromethylated polystyrene containing 3½% of divinylbenzene by treatment with anhydrous dimethylamine in dry dioxan. The few strong-base groups in the product were eliminated by heating the free-base form at 100° under vacuum for 2 hr.[2] The resin had a capacity of 4·10 mequiv./g. of dry chloride form.

The low-capacity strong-base resins were prepared from polystyrene beads containing either 2% or 8% of divinylbenzene. The beads were first allowed to swell in ten times their weight of chloromethyl ether (b. p. 58—59°) for 24 hr. at 4°, stannic chloride catalyst (0·1%) was added, and the beads left for a further 24 hr. at 4°. The mixture was then heated to 50° for periods of between 15 min. and 48 hr., depending upon the final capacity desired. The chloromethylated polystyrene beads were washed with dioxan and aminated by treating them with 25% aqueous trimethylamine at 20° for two days.

RESULTS AND DISCUSSION

Experiments with Amberlite I.R.A. 400.—Application of the law of mass action to the displacement of A^{z-} from an ion-exchange resin by a univalent anion B^-, *i.e.*, to the equilibrium

$$A^{z-}(r) + zB^-(s) \rightleftharpoons zB^-(r) + A^{z-}(s)$$

where (r) refers to the resin and (s) to the solution phase, leads directly to the expression

$$\frac{[B^-(r)]^z[A^{z-}(s)]}{[B^-(s)]^z[A^{z-}(r)]} \cdot \frac{\gamma A^{z-}(s)}{(\gamma B^-(s))^z} = Kd \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where the terms in [square] brackets refer to molalities in either phase and the γ's are ion activity coefficients. Kd is the practical molal selectivity coefficient determined experimentally. In all experiments now described the solutions were very dilute and the solution activity coefficients are taken as unity.

The values of Kd for aurocyanide displacing a number of different ions from the resin (*i.e.*, K_A^{Au}, see above), determined at different gold loadings, are plotted in Fig. 1 against the mole fraction of the resin in the aurocyanide form (X_{Au}). The mean values of Kd (*i.e.*, $K'd$, when $K'd = \int_0^1 Kd \, . \, dX_{Au}$) are given in Table 1. No detailed attempt was made to explain the shape of the Kd curves in Fig. 1 although more regular behaviour is

TABLE 1. *Selectivity coefficients of various anions against aurocyanide on Amberlite I.R.A.* 400.

Type of ion	Ion = A	$K'_A{}^{Au}$	log $K'_A{}^{Au}$
Spherical	F^-	5500	3·74
	Cl^-	692	2·84
	Br^-	165	2·22
	I^-	36	1·56
Linear	CNS^-	9·6	0·98
	$[Ag(CN)_2]^-$	5·75	0·76
	$[Au(CN)_2]^-$	1·0	0·00
Tetrahedral	BF_4^-	26	1·415
	ClO_4^-	4·6	0·66
	MnO_4^-	0·53	−0·28
	ReO_4^-	3·8	0·58
Pyramidal	ClO_3^-	50 *	1·70
	BrO_3^-	195 *	2·29
	IO_3^-	250 *	2·40
Square-planar	$[Ni(CN)_4]^{2-}$	246	2·39
	$[Pd(CN)_4]^{2-}$	76	1·88
	$[Pt(CN)_4]^{2-}$	49·6	1·695
Octahedral	$[Co(CN)_6]^{3-}$	$8·0 \times 10^9$	9·90
	$[Fe(CN)_6]^{3-}$	$6·0 \times 10^9$	9·78

* $K'd$ obtained from $\int_0^{0·5} Kd \, . \, dX_{Au}$

obtained if the exchange takes place between ions of similar type, *e.g.*, linear ions such as $[Au(CN)_2]^-$ and CNS^- where the ratio $\gamma[Au(CN)_2]^-/\gamma CNS^-$ in the resin phase should be approximately constant. The variations found in *Kd* with resin loading may be due to a change in ionic strength in the resin phase as the composition varies between a largely ionic form (*e.g.*, chloride) where the polarisation forces are small and one where the polarisation forces are large, resulting in a high degree of association between the resin sites and the adsorbed ion. The significance of polarisation forces in anionic resin systems is discussed below.

FIG. 1

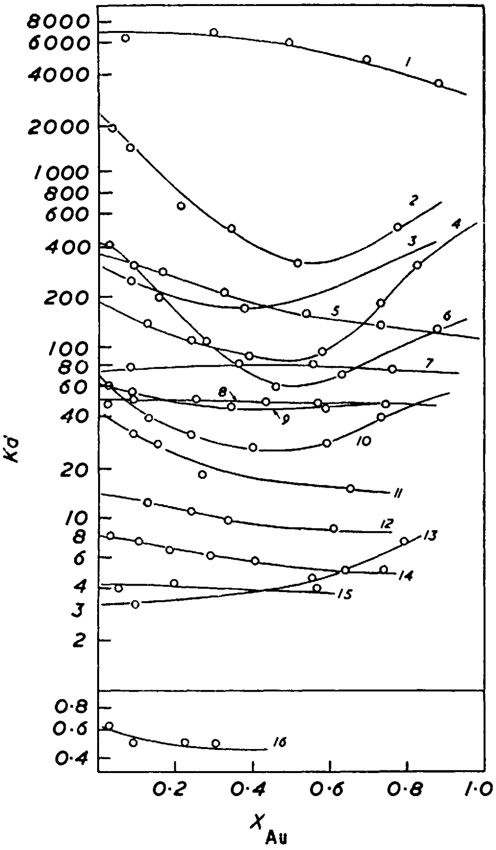
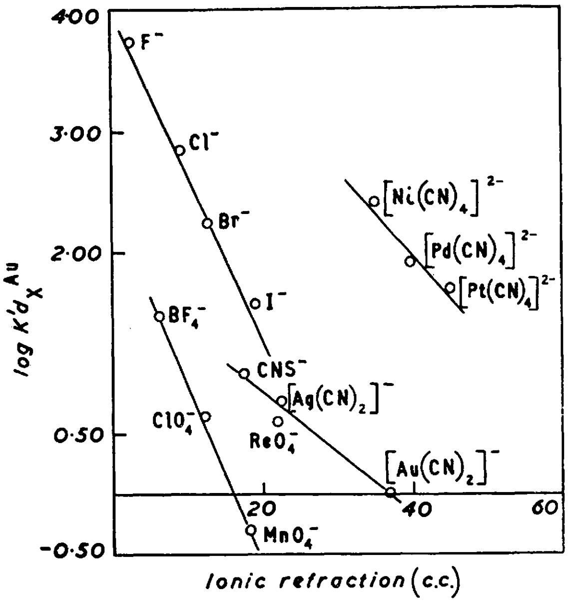


FIG. 2.



1 F^-, 2 Cl^-, 3 $[Ni(CN)_4]^{2-}$, 4 IO_3^-, 5 BrO_3^-, 6 Br^-, 7 $[Pd(CN)_4]^{2-}$, 8 ClO_3^-, 9 $[Pt(CN)_4]^{2-}$, 10 I^-, 11 BF_4^-, 12 CNS^-, 13 ReO_4^-, 14 $[Ag(CN)_2]^-$, 15 ClO_4^-, 16 MnO_4^-.

Most of the selectivity coefficients measured are far from unity and usually vary largely with resin composition.

With a cation-exchange resin Kressman and Kitchener[3] found that the observed equilibria are represented quite well by the law of mass action if concentration is used in place of activities in the resin phase. Moreover, the equilibrium constants for the exchange between ammonium ions and the alkali metals are a function of the hydrated ionic size of the exchanging ions expressed as the a^0 parameter of the Debye–Hückel theory. This leads to preferential adsorption of the ion with the smaller hydrated radius. Apparent exceptions to this relationship, such as occurred with the thallous ion, are explained on the basis of the incomplete dissociation in solution of the salts of the cation concerned. This factor should not normally be important here owing to the exclusive use of the sodium and potassium salts of the anions.

In general it can be considered that there are three main factors operating between a

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[3] Kressman and Kitchener, *J.*, 1949, 1190.

resin functional group and an adsorbed ion: (*a*) coulombic forces, (*b*) polarisation forces, and (*c*) van der Waals forces and ion–dipole interactions. The polarisabilities of cations are usually small, so that with all but the largest cations the coulombic forces are chiefly responsible for the binding of cations to a resin, as has been often confirmed.[3–7] However, Gregor *et al.*[8] showed that the selectivity coefficients obtained on Dowex 2 for the exchange of a given anion with the halide ions is a linear function of the polarisability of the latter as measured by their ionic refractions, their affinity for the resin increasing with increase in their polarisability, *i.e.*, from fluoride to iodide. This suggests that anion-exchange systems are not governed only by coulombic forces as are cation-exchange systems, but that polarisation forces are of major importance. This conclusion has been confirmed and extended here.

In Fig. 2 are plotted values of log *K'd* against the ionic refraction for the ion A^- being displaced from the resin by aurocyanide. The ionic refraction values have been taken from the literature [9] or calculated from the molar refraction in aqueous solution of the sodium and potassium salts of the ions. Except for per-rhenate and the three trigonal-pyramidal ions chlorate, bromate, and iodate (not plotted in Fig. 2) all ions of the same geometrical shape fall on the same straight line. This result is obtained despite the wide spread found in certain cases in the individual *Kd* values from which the averaged *K'd* values were calculated. The high affinity of perchlorate and thiocyanate for the resin, which Gregor *et al.*[8] considered exceptional, are thus explicable by their shape and ionic refraction in the same way as are the affinities of the halide ions. The steep slopes of the lines show that the affinity for the resin of a series of ions of the same shape is not only proportional to, but highly dependent upon, their polarisability. This confirms that polarisation forces are of prime importance in anion exchange, just as are coulombic forces in cation exchange. Thus in cation-exchange systems, owing to the negligible amount of ion-pair formation between the ionised resin sites and the adsorbed cations,[7] no particular cation can be considered as belonging to any particular resin group. This will not be true of anion-exchange processes where, owing to the greater interaction between the resin sites and the adsorbed anions caused by the polarisation forces, ion-pair formation is favoured.

That perrhenate does not fall on the same ionic refraction–selectivity curves as do the other univalent tetrahedral ions (Fig. 2) may be due to its being present in solution partly as the meso-form ReO_5^{3-}. With chlorate, bromate, and iodate the observed discrepancies may be due partly to the fact that the principal and lesser axes of polarisability of these ions appear to become more nearly equal from chlorate to iodate.[10] Also, as these are the only unsymmetrical ions studied here, the ion–dipole forces acting between these ions and the resin sites may oppose the polarisation forces. These ion–dipole forces should decrease from chlorate to iodate owing to the greater electronegativity of the chlorine atom. These two effects reverse the affinity order expected on the basis of ionic refractions, making it $ClO_3^- > BrO_3^- > IO_3^-$.

Thus the greater the degree of interaction between an adsorbed anion and the charged resin sites, *i.e.*, the greater the polarisation forces, the greater the affinity of that anion for the resin. The relatively low selectivity of the resin for the highly polarisable bivalent ions nickel(II) and platinum(II) tetracyanides, and the extremely low values (*ca.* 10^{-10}) obtained with the tervalent cobalt(III) and iron(III) hexacyanides, indicate that these ions interact with the resin much less than do univalent anions of comparable polarisability.

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[4] Gregor and Bregman, *J. Colloid Sci.*, 1951, **6**, 323.

[5] Bauman and Eichlorn, *J. Amer. Chem. Soc.*, 1947, **69**, 2830.

[6] Gregor, *ibid.*, 1948, **70**, 1793.

[7] Glueckauf, *Proc. Roy. Soc.*, 1952, *A*, **214**, 207.

[8] Gregor, Belle, and Marcus, *J. Amer. Chem. Soc.*, 1955, **77**, 2713.

[9] Fajans and Joos, *Z. Physik*, 1924, **23**, 46; Heydweiller, *Physik. Z.*, 1925, **26**, 526; Rogers and Malik, *J. Amer. Chem. Soc.*, 1955, **77**, 6515.

[10] Schaefer and Schubert, *Z. Physik*, 1921, **17**, 509.

This decreased interaction of multivalent anions can be explained if the equilibrium position of the multivalent ion in the resin phase is assumed to be at the " centre of gravity " of the resin cation groups with which it is associated. This would normally cause the average distance between the resin sites and the multivalent anion to be greater than that between a resin site and a univalent anion (which would presumably be equal to the a° distance of the Debye–Hückel theory) and this is the probable cause of the reduced interaction and the lower selectivities found for multivalent than for univalent anions, as observed qualitatively by others. For instance, Kraus and Moore [11] showed that in concentrated hydrochloric acid univalent chloride complexes were more strongly adsorbed by strong-base resins than were multivalent complex chlorides.

The significance of the wide variations in *Kd* obtained here for anions of different charge is shown by comparison with the equilibrium constants found for the exchange of cations of different valency on a sulphonic acid resin. For example, the value given for the equilibrium constant [12] in the exchange of Al^{3+} for NH_4^+ was 4·1, as compared with $7{\cdot}2 \times 10^{-4}$ for the exchange of $[Co(CN)_6]^{3-}$ for $[Au(CN)_2]^-$ now found (calculated by the method in ref. 12). The maximum difference found for the selectivity coefficients for the cations most strongly and least strongly held by the sulphonic acid exchanger was of the order of ten, irrespective of the charges of the two cations; [12] values for the selectivity coefficients as large as 10^{10} have now been obtained with anion-exchange systems. In fact small changes of *Kd* with varying ionic charge of the exchanging ions can be considered as characteristic of an ion-exchange system where coulombic forces are of chief importance, whereas large variations in *Kd* with varying ionic charge of the exchanging ions is characteristic of a system where polarisation forces are of major importance.

The high affinity of Amberlite I.R.A. 400 for the reference ion $[Au(CN)_2]^-$, and its application to the extraction of gold from cyanide liquors,[1] is due to the high polarisability and linear shape of the aurocyanide ion. With a linear ion the major axis of polarisability will be along its length, so that the polarisation forces will be concentrated in this direction. No such concentration in a given direction can take place in spherical ions such as chloride, and it is significant that all three linear ions used had a high affinity for the resin. The rapid increase in the selectivity of the resin for aurocyanide compared with ions such as chloride or bromide as the mole fraction of gold in the resin phase (X_{Au}) tends to zero (Fig. 1) is compatible with the view of Burstall *et al.*[1] that the aurocyanide loading of Amberlite I.R.A. 400 should not exceed 0·3 mequiv./g. of resin (*i.e.*, $X_{Au} = 0{\cdot}1$) if base metals are to be selectively eluted before gold.

Now if the resin sites and the adsorbed anions interact through polarisation forces, then the greater the degree of interaction the smaller will be the effective concentration of free ions in the resin phase. As the degree of swelling of a resin in contact with an aqueous solution is proportional to the concentration of free ions in the resin phase, as is apparent from the Donnan membrane equilibrium, then the swelling obtained with different ionic forms of the resin in equilibrium with solutions of equivalent concentrations will vary inversely with the polarisability of the ion. Support for this comes from the data given by Gregor, Belle, and Marcus [13] for the stoicheiometric molalities (*i.e.*, molalities per 1000 g. of water in the resin phase) for various univalent ions adsorbed on a strong-base polystyrene resin containing 8% of divinylbenzene from 0·01N-equilibrating solutions. When these molalities are plotted against their ionic refractivities straight lines are obtained (Fig. 3). The halide ions lie on one straight line with nitrate, hydroxide, and thiocyanate near, but significantly off, the curve, thus again illustrating the effect of ionic shape on the polarisation forces. Perchlorate lies considerably above the halide line, thus confirming the exceptionally high polarisation forces existing between a tetrahedral ion and an anionic resin. Acetate and the three chloro-acetates lie along a second straight line, whilst

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[11] Kraus and Moore, *J. Amer. Chem. Soc.*, 1951, **73**, 10.

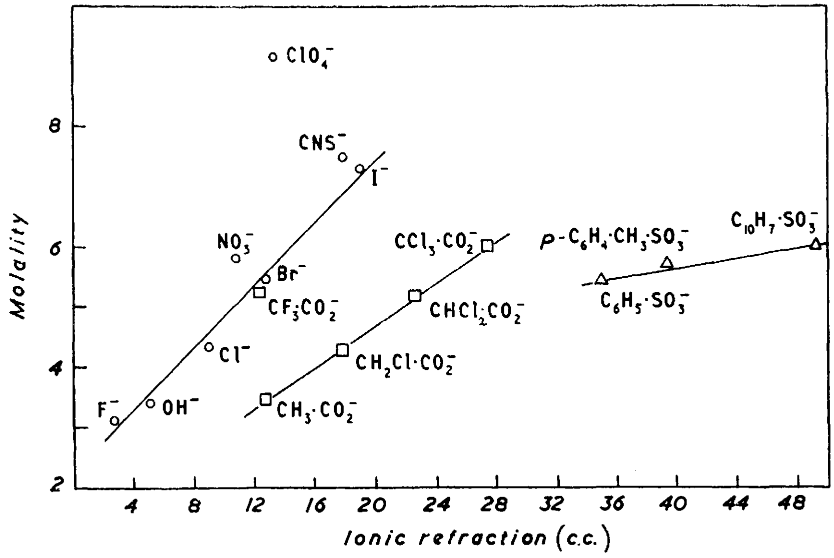
[12] Kressman and Kitchener, *J.*, 1949, 1208.

[13] Gregor, Belle, and Marcus, *J. Amer. Chem. Soc.*, 1954, **76**, 1984.

benzenesulphonate, toluene-*p*-sulphonate, and β-naphthalenesulphonate fall along a third. Trifluoroacetate, however, falls on the halide curve. The fact that three separate straight lines are obtained indicates that the degree of interaction between the charged resin sites and the adsorbed ions is affected by both the shape of the ion and its chemical nature as well as by its polarisability. With β-naphthalenesulphonate, for example, most of the measured refractivity is due to the organic part of the molecule, so that the anion might not be expected to be so greatly affected by a charged resin site as would a purely inorganic anion. This effect appears to be general, increase in the purely organic content of the adsorbed anion moving the stoicheiometric molality–refractivity curves to the right and decreasing their slope, *i.e.*, showing a decreased interaction between the resin sites and the adsorbed anions at any given value of the refractivity of the adsorbed anion.

Weak-base Resins.—Preliminary experiments with a weak-base resin (J.A. 1) containing benzyldimethylamine groups, with solutions containing potassium auro- and argento-cyanides (*ca.* 10^{-3}M) and 0·003M-potassium cyanide (pH 10·3), gave a mean value for the selectivity coefficient $K_{\mathrm{Ag}}{}^{\mathrm{Au}}$ of 8·3. This is very near the value found with Amberlite I.R.A. 400 at low gold loadings (Fig. 1), and suggests that the selectivity coefficients obtained for exchange of univalent anions are approximately the same on a weak-base as on a strong-base resin. This is expected, as a univalent anion can approach a resin site until it reaches the equilibrium a° distance, irrespective of the spacing of the active groups in the resin matrix. However, owing to the low degree of ionisation of a weak-base resin in alkaline solution, and also to the prevention of "clustered" ionisation by the inductive effect, the resin sites will be widely spaced throughout the resin matrix, so that multivalent anions, on the assumption that they come to their equilibrium position at the "centre of gravity" of the ionised resin sites, will be more distant from these resin sites than they would be in a strong-base resin. The tendency for the displacement of multivalent by univalent anions from a weak-base resin in alkaline solution will thus be greater than with a strong-base resin in a similar environment.

FIG. 3.



The greater selectivity of weak-base resins for aurocyanide over the multivalent base-metal cyanides in alkaline cyanide media than of Amberlite I.R.A. 400 (see ref. 2) is considered to be mainly due to the mass-action effect due to the decreased resin capacity (see p. 239) and the increased value of the selectivity coefficients for gold displacing base-metal cyanides from the resin due to the decreased number of resin sites available for exchange as discussed above.

Low-capacity Strong-base Resins.—The selectivity for aurocyanide in alkaline cyanide solution containing multivalent base-metal cyanides is relatively greater for a weak-base than for a strong-base resin owing to the fewer resin sites available in the former under these conditions. If this explanation is correct the selectivity for gold should be similarly increased simply by reducing the capacity of a strong-base exchanger. In order to test this postulate a series of strong-base resins was prepared with capacities ranging from 0·8 to 4·5 mequiv./g. of dry chloride form and containing either 2% or 8% of divinylbenzene as cross-linking agent. Also included in the Table 2 are the volumes of 1 g. of the chloride form of the resin when loaded with complex metal cyanides and the capacity of the resin per c.c. of this final loaded form. The loadings of gold and base metals in Table 2 were obtained by treating 1 g. columns of resin with a solution containing 6 mg. of Au, 50 mg. of Ni^{II}, 30 mg. of Cu^{I}, 24 mg. of Fe^{II} (all as complex cyanides), 150 mg. of sodium cyanide, and 160 mg. of sodium thiocyanate per litre, the technique previously described [2] being used.

TABLE 2. *Adsorption of gold and base-metals from cyanide solutions by strong-base resins of various capacities.*

Resin	Divinyl-benzene (%)	Capacity (mequiv./g.) in dry chloride form	Volume of 1 g. of Cl-form of resin when loaded with complex cyanides (c.c.)	Capacity per c.c. of resin when loaded with complex cyanides (mequiv.)	Metal loading in mg./g. of dry Cl-form			
					Au	Ni	Cu	Fe
AX 15	8	0·87	1·03	0·845	6·7	15·0	3·3	0·9
AX 18	8	1·62	1·25	1·29	8·7	32·5	6·0	3·0
AX 19	8	3·56	1·48	2·40	8·7	67·5	9·6	10·0
AX 21	2	0·96	1·10	0·87	4·2	14·0	2·0	1·6
AX 22	2	1·76	1·37	1·28	4·5	33·0	5·7	4·5
AX 23	2	2·30	1·40	1·65	6·0	40·0	6·9	5·7
AX 24	2	4·46	1·42	3·15	11·3	72·5	11·3	24·1

Table 2 shows that some selectivity for aurocyanide is obtained, although the total gold loadings are not so high as on weak-base resins.[2] A more rigid interpretation of the data in Table 2 is given below.

For the displacement of a bivalent anion (B^{2-}) from a strong-base resin by aurocyanide the following equation can be written, the solution phase being assumed dilute

$$\frac{[\mathrm{Au(r)}]^2[\mathrm{B}^{2-}(\mathrm{s})]}{[\mathrm{Au(s)}]^2[\mathrm{B}^{2-}(\mathrm{r})]} = K^\circ \cdot \frac{f\mathrm{B(r)}}{[f\mathrm{Au(r)}]^2} = Kdm \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where the terms in square brackets refer to molarities in the resin phase (*i.e.*, moles/l. of swollen resin) and in solution, fB(r) and fAu(r) are the molar activity coefficients of B^{2-} and $[Au(CN)_2]^-$ in the resin phase, K° is the thermodynamic equilibrium constant, and *Kdm* is the molar selectivity coefficient. Molarities in the resin phase, rather than molalities, are used here as it is now the volume characteristics of the system which are being considered.

For a given resin, in this case Amberlite I.R.A. 400, log *K'd* is proportional to the ionic refraction of the ion being displaced from the resin by the reference ion, aurocyanide. We are now considering the displacement of a bivalent ion B^{2-} by the univalent aurocyanide ion. If we assume *K'd* and *Kdm* to be simply related, $\log_{10}Kdm$ will be directly proportional to the ionic refraction of B^{2-} and hence to its polarisability. Thus

$$\log_{10}Kdm = b' - a'[R] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where b' and a' are constants and $[R]$ is the ionic refraction of B^{2-}. If, however, we study a specific exchange so that $[R]$ remains constant but vary the capacity of the resin in order to alter the distance d between the bivalent ion and the resin sites, and hence both the total polarisation forces acting on the ion and the interaction energy between the resin sites and the ion, we can write eqn. (3) as

$$\log_{10} Kdm = b - aP \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where P is the energy of interaction between the charged resin sites due to the polarisation forces and will vary inversely as the fourth power of the distance d between them,[14] and a and b are constants. Now d will be proportional to the distance d^1 between adjacent resin sites, d^1 itself being proportional to the cube root of the resin capacity on a volume basis. Thus $P \propto 1/d^4$ so

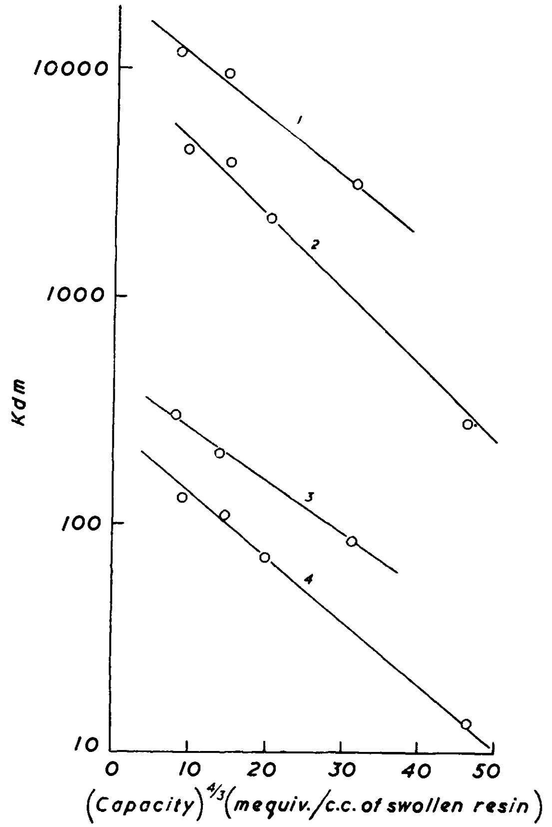


Fig. 4.

1. $Kdm_{Cu}{}^{Au} \times 10^{-6}$, 8% divinylbenzene.
2. $Kdm_{Cu}{}^{Au} \times 10^{-6}$, 2% ,,
3. $Kdm_{Ni}{}^{Au} \times 10^{-1}$, 8% ,,
4. $Kdm_{Ni}{}^{Au} \times 10^{-1}$, 2% ,,

$$P \propto (\text{Capacity})^{\frac{4}{3}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and on substituting in eqn. (4) we get

$$\log Kdm = b - E\ (\text{Capacity})^{\frac{4}{3}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The molar selectivity coefficient *Kdm* should thus vary logarithmically with the $\frac{4}{3}$ root of the resin capacity on a volume basis. Values of *Kdm*, calculated from Table 2, are

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[14] Hirschfelder, Curtiss, and Bond, "Molecular Theory of Gases and Liquids," John Wiley and Sons, New York, 1954.

thus plotted in Fig. 4. The approximate linearity of the plots for resins with the same degree of cross-linking is strong evidence that the greater selectivities of weak-base resins for aurocyanide in alkaline cyanide solution than of a normal strong-base resin, are largely due to the smaller number of resin sites available (decreased charge density of the resin) in the former.

The selectivity shown for aurocyanide by weak-base resins in alkaline solution, and for aurocyanide by low-capacity strong-base resins, is due to aurocyanide's being univalent and able to interact strongly with the resin sites irrespective of their distribution in the resin matrix. Similar more selective behaviour would be shown by these resins for any univalent anion than for multivalent anions, although the effect is magnified with aurocyanide owing to its naturally high affinity for the resin. This selectivity for univalent anions will only be exhibited by weak-base resins in alkaline media when they will be only slightly ionised. They will not be selective in acid solution when they will be fully ionised and thus resemble a normal strong-base resin. The low-capacity strong-base resins, however, will be more selective for univalent than for multivalent ions in both acid and alkaline media. For example, a low-capacity strong-base resin should be selective for per-rhenate (which has a high affinity for the resin, see Fig. 1) in acid solution, whereas a weak-base resin would not.

In addition to the effect of charge density upon selectivity, the actual ratio of gold to multivalent base-metal cyanide on a resin will vary on altering the capacity, even though *Kd* for the exchange may remain constant. Thus it is well known that for exchange between ions of different charge the position of equilibrium, that is, the ratios of the molarities of the two ions in the resin phase, depends not only on the molarities in solution, but also on the total solution concentration. The effect of diluting the aqueous phase is to cause more of the ion of higher valency to pass into the resin. Similarly dilution of the resin phase (*i.e.*, decrease in the capacity) will cause more of the ions of the lower valency to pass into the resin with an apparent increase in selectivity, although, other factors being equal, *Kd* for the reaction will remain constant. This effect is usually referred to as the " mass action " effect.

This paper is published by permission of the Director of the Chemical Research Laboratory. We thank Mr. D. Reichenberg, M.Sc., for resin samples used in initial experiments.

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[*Received, May* 28*th*, 1957.]