891. *The Reaction of the Benzenediazonium Ion with Certain Anions in Aqueous Acid Solution.*

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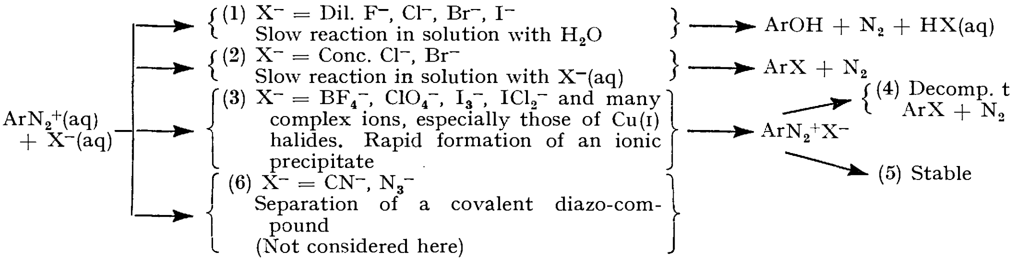
The reaction of the benzenediazonium ion with a number of univalent anions in aqueous acid solution is discussed. A correlation exists between the type of behaviour displayed (phenol or phenyl halide formation, or the precipitation of diazonium salts) and the anionic radius.

THE classification of arenediazonium salt reactions in *acid* solution (in which attention can justifiably be restricted to the diazonium cation) is usually based solely on the type of product obtained.[1] Little attention has been paid to the importance of the precipitation of unstable intermediates as a factor governing the products. That this occurs when it is not suspected because of the deep colour of the reaction mixture and the vigorous effervescence, is shown by the recent work of Carey, Jones, and Millar.[2] They found that unstable diazonium tri-iodides are precipitated when cold solutions of diazotized aniline and other aromatic primary amines containing a slight excess of nitrous acid, are added to solutions of potassium iodide. It has also been observed [3] that in the presence of urea (which would prevent the oxidation of iodide to tri-iodide) the formation of aryl iodide from the arenediazonium cation in potassium iodide solution is extremely slow.

With certain reservations discussed below, it appears that the formation of a precipitate is crucial to the type of product obtained because in such cases the diazonium ion is removed from the influence of the water. Thus Millar [2] has found that although *o*-toluenediazonium iodide can be precipitated, yet if redissolved in water and boiled it gives 99% of *o*-cresol.

The various products can therefore arise from the following alternative reactions:



Much controversy [4] has centred round the mechanism by which unstable intermediates decompose. The treatment here, however, is concerned only with the factors which predispose the system towards unstable intermediates: it cannot distinguish between alternative mechanisms by which they decompose.

(1) *Thermodynamics of the Formation of Phenol and of Phenyl Halides.*—Table 1, constructed from values of ΔG°_{298}(f) given in Table 5, suggests that from benzenediazonium and halide ions in dilute solution the thermodynamically stable products are phenol and nitrogen. In fact, actual values of ΔG_{298} (hydrolysis) depend on concentrations, particularly on those of the hydrogen ion and of the halide ion. However, only for concentrated hydrochloric, hydrobromic, and hydriodic acids can the concentrations and the activity coefficients be sufficiently high for ΔG_{298} (hydrolysis) to become zero or positive. [Concentrated HCl, $\sim$ 11m, $\gamma_{\pm} \sim 13{\cdot}5$, and ΔG_{298} (hydrolysis) ~ 0; concentrated KI, $\sim 7{\cdot}5$m, $\gamma_{\pm} \sim 0{\cdot}9$, and ΔG_{298} (hydrolysis) $\sim -1{\cdot}5$ kcal. mole^{-1}.] These values of ΔG

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[1] Saunders, " The Aromatic Diazo Compounds and their Technical Application," Arnold, London, 2nd edn., 1949; Cowdrey and Davies, *Quart. Rev.*, 1952, **6**, 358.

[2] Carey, Jones, and Millar, *Chem. and Ind.*, 1959, 1018; Carey and Millar, *ibid.*, 1960, 97.

[3] Carey and Millar, unpublished results; cf. Hickinbottom, " Reactions of Organic Compounds," Longmans Green. London, 3rd edn., 1957, p. 488.

[4] Cowdrey and Davies, ref. 1, p. 370.

(hydrolysis) show that the resistance of phenyl halides to hydrolysis in an acid solution must be governed by kinetic factors. It follows that the relative amounts of phenol and of phenyl halide formed from diazonium salts are not governed by equilibrium considerations.

TABLE 1.

Reactants	$PhN_2^+(aq) + X^-(aq) + H_2O(l)$				
Products	$PhOH(l) + H^+(aq) + X^-(aq) + N_2(g)$	$PhX(l) + N_2(g) + H_2O(l)$			
		X = F	X = Cl	X = Br	X = I
ΔG°_{298} (kcal. mole^{-1})	$-62{\cdot}5$ ($-66{\cdot}9$ if X = F and if HF is considered undissociated)	$-62{\cdot}3$	$-56{\cdot}5$	$-54{\cdot}4$	$-58{\cdot}7$
$K_{\text{hydrol.}}$ (PhX)		$2{\cdot}8 \times 10^3$ *	$2{\cdot}5 \times 10^4$	$8{\cdot}7 \times 10^5$	$7{\cdot}2 \times 10^2$

* HF considered undissociated.

The reason why phenol is always formed in large excess from diazonium salt solutions is that it is formed faster than phenyl halides. This might be thought due purely to the large excess of water present. However, it is known that in most cases neither the rate of formation nor the yield of a halogenobenzene is significantly changed by increasing the concentration of halide salts [5] (mean ionic activity coefficients do not exceed 1·0 in contrast to the concentrated solutions of the hydrogen halides cited above). This is not to be expected if the halide ion and water are competing only on a concentration basis.

We believe the underlying reason for the preferential formation of phenol under these conditions to be as follows. Whatever the mechanisms of the alternative reactions, it is clear that one of the steps must involve the reaction between a hydrated benzenediazonium ion and either a hydrated anion or a hydrated, *i.e.*, hydrogen-bonded, water molecule. Both cases would involve breaking bonds of hydration, and it is to be expected that the preferential formation of phenol from aqueous solutions will be inversely correlated with the relative sizes of the absolute enthalpies and free energies of hydration given in Table 2.

TABLE 2. *Enthalpies and free energies of hydration of univalent anions at 25°.*

	F^-	Cl^-	Br^-	I^-	BF_4^-	ClO_4^-	I_3^-	H_2O [a]
ΔH°_{298} (abs. hydration)...	$-121{\cdot}9$	$-87{\cdot}6$	$-79{\cdot}8$	$-69{\cdot}7$	$-71{\cdot}2$	$-57{\cdot}1$	$-43{\cdot}8$	$-10{\cdot}5$
ΔG°_{298} (abs. hydration) ...	$-112{\cdot}5$	$-82{\cdot}3$	$-75{\cdot}2$	$-67{\cdot}1$	$-65{\cdot}8$	?	?	$-2{\cdot}05$
Effective radius [b] (Å) ...	1·36	1·81	1·95	2·16	2·26	2·45	3·0	—

[a] Values for vaporisation. [b] For details see section 3.

These can be taken as a measure of the difficulty of removing a participating ion from the surrounding water molecules. The values of absolute free energy of hydration are based on Gurney's value of $-5{\cdot}5$ cal. deg.$^{-1}$ for the absolute entropy of hydration of the proton, and an absolute enthalpy of hydration [6] of -261 kcal. mole^{-1}.

The free energies of hydration of singly charged anions differ primarily because of differences in ion–dipole interaction. There is thus a correlation between phenol formation and anionic radius.

(2) *Precipitation of Solid Benzenediazonium Salts.*—The effective anionic radius is also the controlling factor for precipitation. The solubility of an electrolyte is governed by enthalpy and entropy changes accompanying dissolution. For a uni-univalent electrolyte the solubility (molality m) at a temperature $T°$ K is given by:

$$\begin{aligned} -\boldsymbol{R}T \ln (m\gamma_\pm)^2 &= \Delta H^\circ \text{ (soln)} - T\Delta S^\circ \text{ (soln)} \\ &= \Delta H^\circ \text{ (hydration of ions)} - \Delta H^\circ \text{ (lattice)} - T\Delta S^\circ \text{ (soln)} \end{aligned}$$

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[5] Gasiorowski and Waÿss, *Ber.*, 1885, **18**, 1936; Hodgson and Sibbald, *J.*, 1945, 545; Bunnett. *Quart. Rev.*, 1958, **12**, 1.

[6] Halliwell and Nyburg, unpublished work.

It has long been known that both lattice energies, $\Delta U_0{}^\circ$ (lattice), and hydration energies, $\Delta U_0{}^\circ$(hyd), of ionic crystals are explicable in terms of ionic radius and charge. Kapustinski [7] has used this approach semiempirically, and Yatsimirski [8] has extended and summarized his work. We have applied the method to evaluating lattice and hydration *enthalpies* at 25° C. We find that for uni-univalent salts, whatever the crystal structure, lattice enthalpies at 25° are given, for most salts within 1—2 kcal mole^{-1}, by the empirical equation

$$-\Delta H^\circ_{298}\ (\text{lattice}) = \frac{600}{r_1 + r_2}\left(1 - \frac{0\cdot4}{r_1 + r_2}\right)\ \text{kcal. mole}^{-1} \quad . \quad . \quad . \quad (1)$$

where r_1 and r_2 (in Å) are cationic and anionic radii respectively (for details of radii see section 3). The reason why one equation applies to such a wide variety of crystal structures has been discussed elsewhere.[7,9] The curve corresponding to eqn. (1) is plotted in Fig. 1.

FIG. 1.

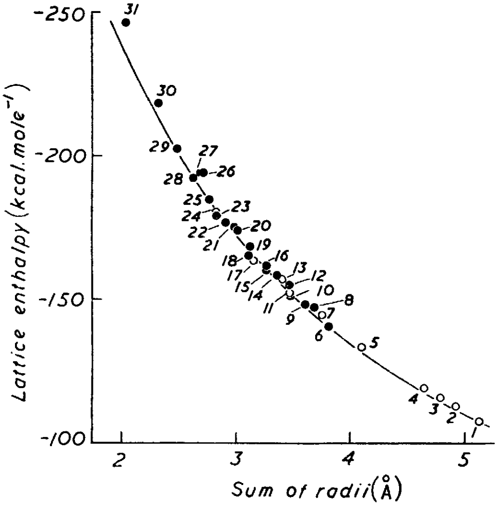

FIG. 2.

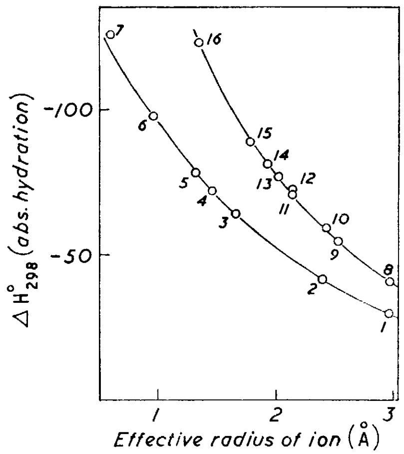

FIG. 1. *Lattice enthalpies (ΔH°_{298}; kcal. mole^{-1}) (plotted against the sum of the effective ionic radii ($r_1 + r_2$) (Å) for uni-univalent salts at 25°.*

1, NMe_4I. 2, NMe_4Br. 3, NMe_4Cl. 4, CsI_3. 5, $CsClO_4$. 6, CsI. 7, CsN_3. 8, CsBr. 9, $KClO_4$.
10, KI. 11, $KBrF_4$. 12, CsCl. 13, KN_3. 14, $NaClO_4$. 15, KCN. 16, KBr. 17, $NaBF_4$.
18, NaI. 19, KCl. 20, CsF. 21, NaN_3. 22, NaBr. 23, LiI. 24, $LiBrF_4$. 25, NaCl. 26, LiN_3.
27, KF. 28, LiBr. 29, LiCl. 30, NaF. 31, LiF.

● *Enthalpies given before this work.* ○ *Estimated enthalpies (see Table 6). The continuous line represents eqn. (1).*

FIG. 2. *Absolute enthalpies of hydration of univalent ions at 25°.* $\Delta H^\circ_{298}(\text{hydration})H^+,g = -261$ *kcal. g.-ion^{-1}.*

1, $NMe_4{}^+$. 2, $PhN_2{}^+$. 3, Cs^+. 4, Rb^+. 5, K^+. 6, Na^+. 7, Li^+.
8, $I_3{}^-$. 9, $Ph{\cdot}SO_3{}^-$. 10, $ClO_4{}^-$. 11, I^-. 12, $BF_4{}^-$. 13, $N_3{}^-$. 14, Br^-, CN^-. 15, Cl^-. 16, F^-.

The allocation of individual absolute ionic hydration enthalpies is made difficult by lack of agreement on the value of the absolute hydration enthalpy of the proton. If the value -261 kcal. mole^{-1} is used, absolute enthalpies of hydration of cations and of anions converge with increasing ionic radius in satisfactory agreement with theory [10] (see Fig. 2).*

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* Values of ΔH(abs.hyd)$/z^2$ for multivalent ions with inert-gas structures also lie on these curves.

[7] Kapustinski, *Z. phys. Chem.*, 1933, *B*, **22**, 257; see also *Quart. Rev.*, 1956, **10**, 283; Kapustinski and Yatsimirski, *Zhur. fiz. Khim.*, 1948, **22**, 1271.

[8] Yatsimirski, " Thermochemie von Komplex Verbindungen," Academie-Verlag, Berlin, 1956, Chap. 6.

[9] Pauling, " Nature of the Chemical Bond," Cornell, Ithaca, 1944, Chap. 10.

[10] Buckingham, *Discuss. Faraday Soc.*, 1957, **24**, 151.

Fig. 3*a* relates the enthalpy of solution of an ionic salt, calculated from Figs. 1 and 2 in terms of the radii of the constituent ions. Fig. 3*b* gives the experimental enthalpy values for specific salts. (For discussion of the ClO_4^- values see Table 5, footnote *k*.) The effective radius of the benzenediazonium ion has been taken as 2·4 Å (see section 3). This allows a curve to be drawn on Fig. 3*b* for which enthalpies of solution can be read off for the required benzenediazonium salt.

Fig. 3.

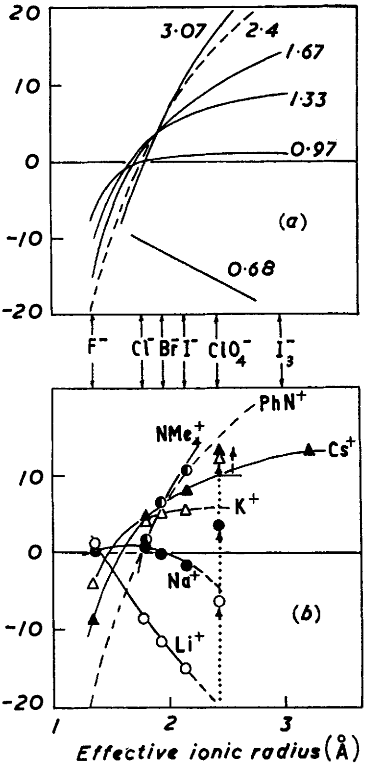

Fig. 4.

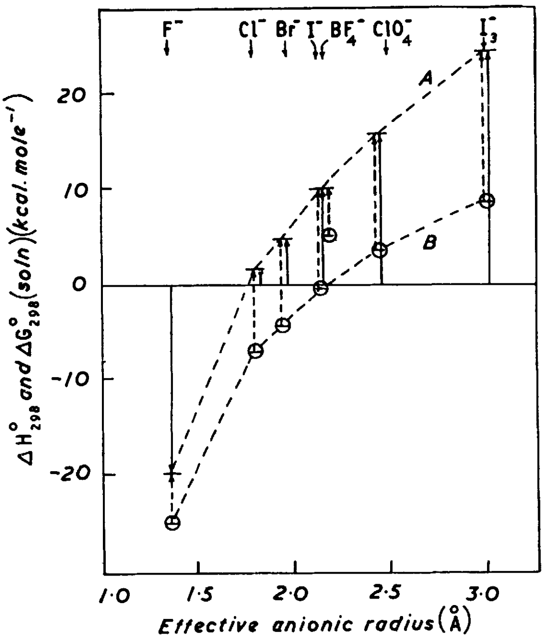

Fig. 3. *Comparison, for uni-univalent salts, of* (*a*) *values of* ΔH°_{298} (soln) *calculated from lattice and hydration enthalpies and* (*b*) *experimental values of* ΔH°_{298} (soln). *In each diagram the broken line refers to values estimated for benzenediazonium salts. Figures alongside the lines in* (*a*) *are* r_+ (*in* Å). (*See text for comment on the anomalous enthalpies of solution of perchlorates as indicated by dotted lines.*)

Fig. 4. *Estimated values of* ΔH°_{298} (soln) *and* ΔG°_{298} (soln) *of benzenediazonium salts, showing the significance of anionic radius for precipitation.*

A, ΔH°_{298} (soln) *trend.* *B*, ΔG°_{298} (soln) *trend.* *Full vertical lines denote* ΔH°_{298} (soln); *broken vertical lines denote* $T\Delta S^\circ_{298}$ (soln).

Entropy changes on dissolution have been estimated by Kapustinski and Yatsimirski's method [7,8] and are given in Table 3.

Table 3. *Estimated values of* $T\Delta S^\circ$ (soln) *at* 25°C *for various benzenediazonium salts.*

Benzenediazonium salt	F^-	Cl	Br^-	I^-	BF_4^-	ClO_4^-	I_3^-
	increasing ionic radius →						
$T\Delta S^\circ$ (soln) in kcal. g.-ion^{-1}	5	8	9	11	5	13	14

The figure for the borofluoride ion needs comment. Both the estimated and the measured values of $T\Delta S^\circ$ (soln) are less positive than would be expected by comparison

[11] Frank and Wen-Yang Wen, *Discuss. Faraday Soc.*, 1957, **24**, 133.

TABLE 4. *Comparison of* ΔG°_{298} (soln), *estimated from effective ionic radius, with that calculated from solubility data.*

		$PhN_2^+ClO_4^-$	$PhN_2^+BF_4^-$
Solubility (molal)	(i) as reported	0·07m at 0° C [12]	" with difficulty " [9]
	(ii) estimated for 25° C by comparison with solubility curves of other perchlorates, etc.	0·20m	0·05—0·1m
$\gamma_\pm$ at saturation	(estimated [14])	0·7	0·8
ΔG°_{298} (soln) (kcal. mole^{-1})	(i) from solubility	+2·2	+3·5 to +4·0
	(ii) estimated by ΔH° and $T\Delta S^\circ$ terms from ionic radius	+3·0	+5·0

TABLE 5.

	ΔH°_{298}(f)	ΔG°_{298}(f)		ΔH°_{298}(f)	ΔG°_{298}(f)
	(kcal. g.-formula^{-1})			(kcal. g.-formula^{-1})	
PhF(g)	−26·48 [a]	−15·12 [a]	N_3^-(g)	34·8 [i]	—
PhF(l)	−38·23 [a]	−19·27 [a]	N_3^-(aq)	65·53 [i]	83·23
PhCl(g)	12·38 [a]	23·58 [a]			
PhCl(l)	2·55 [a]	21·12 [a]	LiN_3(c)	2·58 [i]	18·50
PhBr(g)	25·30 [a]	33·12 [a]	NaN_3(c)	5·08 [i]	23·76
PhBr(l)	14·1 [a]	30·0 [a]	KN_3(c)	−0·33 [i]	18·04
PhI(g)	35·5 [b]	41·9 [b]	CsN_3(c)	−2·37 [i]	—
PhI(l)	23·05 [b]	37·96			
$Ph{\cdot}NH_2$(l)	7·34 [c]	35·40 [c]	$LiBF_4$(c)	−415·8	—
$Ph{\cdot}OH$(l)	−36·17 [d]	−10·23 [d]	$NaBF_4$(c)	−417·8	—
$Ph{\cdot}OH$(c)	−38·90 [d]	−11·53 [d]	KBF_4(c)	−428·4 [j]	—
$Ph{\cdot}N_2^+$(aq)	90 [e]	109 [f]	BF_4^-(g)	−400 [j]	—
NMe_4^+(aq)	x	y	ClO_4^-(g)	−80·5 [k]	—
NMe_4^+(g)	$(x + 134{\cdot}1)$ [g]	—	CN^-(g)	10 [l]	—
NMe_4Cl(c)	$(x - 41{\cdot}1)$ [g]	—	I_3^-(g)	78·6 [m]	—
NMe_4Br(c)	$(x - 34{\cdot}9)$ [g]	—	I_3^-(aq)	−12·14	
NMe_4I(c)	$(x - 23{\cdot}4)$ [h]	$(y - 14{\cdot}7)$ [h]	NO_2^-(aq)	—	−8·25 [n]

[a] Values recalculated and chosen to be consistent with: heats of combustion,[o,p] vapour-pressure equations,[p] theoretical calculations of thermodynamic functions [q] and third-law entropy values. [b] Using Skinner's best value [s] and then *via* refs. *r* and *t*. [c] Ref. *u*. [d] Ref. *t* and " International Critical Tables." [e] ΔH° (soln) of $Ph{\cdot}NH_2$(l) in HCl(aq) estimated as −7 kcal. mole^{-1}. ΔH (diazotization) = −22·7 kcal. mole^{-1} (ref. *v*). [f] $\bar{S}^\circ(NMe_4^+, aq) = 49{\cdot}5$ cal. deg.$^{-1}$ mole^{-1} (ref. *w*). $\bar{S}^\circ(Ph{\cdot}N_2^+, aq)$ estimated as 52·4 cal. deg.$^{-1}$ mole^{-1} by Cobble's method.[x] Hence $\Delta S^\circ(f)(Ph{\cdot}N_2^+, aq) = -93{\cdot}0$ cal. deg.$^{-1}$ mole^{-1}. [g] Only heats of solution have been measured.[y] Yatsimirski gives r (cation) = 3·0 Å. All are in agreement with ΔH(soln) of NMe_4^+(g) = 28 kcal. g.-ion^{-1}, on which assumption the data have been calculated. [h] Ref. *z* gives ΔH (soln) and ΔS (soln). These are also in agreement with data used in *g* above. [i] Refs. 16 and *w*. [j] Recalc. from thermochemical data.[17,aa] The value adopted here for KBF_4(c) differs only slightly from that given by Altshuller.[bb] [k] For no acceptable value of r do the values of ΔH (soln) predicted from Figs. 2 and 3 agree with experimental values.[y,cc] The discrepancy is less with larger cations as is indicated in Fig. 4. It is important to note that extrapolation suggests that when r (cation) > 2·0 Å, the discrepancy is negligible: the approximate prediction of ΔH (soln) of benzenediazonium perchlorate is not therefore affected. [l] Ref. 22. From Figs. 2 and 3 one obtains lattice enthalpies in good accord with such ΔH (soln) values as are recorded. [m] Most consistent figure from established values of $\Delta H^\circ(f)$ of simple alkali-metal halides and dissociation enthalpies.[dd] [n] Latimer, " Oxidation States," Prentice-Hall, New York, U.S.A., 2nd edn., 1952.

[o] Skinner, *Trans. Faraday Soc.*, 1951, **47**, 254; Hubbard, *J. Phys. Chem.*, 1954, **58**. 396. [p] Smith, Bjellerup, Krook, and Westermark, *Acta Chem. Scand.*, 1953, **7**, 65. [q] Scott, McCullough, Good, Messerly, Hossenlopp, Frow, and Waddington, *J. Amer. Chem. Soc.*, 1956, **78**, 5463; Whiffen, *J.*, 1956, 1350. [r] Stull, *J. Amer. Chem. Soc.*, 1937, **59**, 2726. [s] Skinner, *Roy. Inst. Chem. Monograph*, No. 3, 1958, p. 24. [t] Lange, " Handbook of Chemistry," Handbook Publ. Co., Sandusky, Ohio, U.S.A., 1956. [u] Parks and Huffmann, " The Free Energies of Some Organic Compounds," Chem. Catalog. Co., New York, 1932, p. 188. [v] Wojciechowski, *Bull. Intern. Acad. Polonaise, Classe sci. math. nat.*, 1934, *A*, p. 280. [x] Cobble. *J. Chem. Phys.*, 1953, **21**, 1451. [y] Askew, Bullock, Smith, Tinkler, Gatty, and Wolfenden. *J.*, 1934, 1368. [w] Buchner, *Rec. Trav. chim.*, 1950, **329**, 60. [z] Coulter, Pitzer, and Latimer, *J. Amer. Chem. Soc.*, 1940, **62**, 2845. [aa] Greenwood and Martin, *Quart. Rev.*, 1954, **8**. 1; " Selected Values of Chemical Thermodynamic Properties. Series III." Nat. Bur. Standards, Washington, U.S.A. 1956; Lewis and Randall, " Thermodynamics," McGraw-Hill, New York, U.S.A., 1923, p. 73. [bb] Altshuller, *J. Amer. Chem. Soc.*, 1955, **77**, 6187. [cc] Smeets, *Natuurw. Tijdschrift* 1933, **15**, 105. [dd] Foot, Bradley, and Fleischer, *J. Phys. Chem.*, 1938, **37**, 21.

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[12] Hofmann and Arnoldi, *Ber.*, 1906, **39**. 3146.

[13] Wilke-Dörfurt and Balz, *Ber.*, 1927, **60**, 116.

[14] Robinson and Stokes, " Electrolyte Solutions," Butterworths, London, 1955, p. 250.

with values for other salts. This seems to be the major cause of the insolubility of borofluorides compared with iodides which, on grounds of size and charge, they would be expected to resemble. On dissolution in water, large univalent ions have, on the whole, an overall structure-breaking effect [11] which leads to a more positive value of ΔS° (soln). Hydrogen-bonding between the fluoride and the oxygen atoms would undoubtedly lessen the structure-breaking effect and would explain the lower positive entropy of solution of borofluoride. It is unlikely that such an interaction would greatly affect the enthalpy of solution.

From Figs. 1—3 and Table 3, we have estimated ΔG° (soln) for the benzenediazonium salts under discussion. The results are plotted in Fig. 4 so as to show the contribution of ΔH° and of $T\Delta S^\circ$ in each case. These calculations are in general agreement with the trend of observed solubilities and they predict * that the critical anionic radius for precipitation is about 2·2 Å. Ions smaller than this are predicted to give rise to soluble benzenediazonium salts; larger ions should give insoluble salts. For this reason benzenediazonium perchlorate is expected to have borderline solubility, as indeed should benzenediazonium borofluoride for reasons given above. Table 4 gives the experimental and predicted solubilities of these two salts. The agreement is gratifying.

Summarizing, we see that, apart from certain expected anomalous entropy effects, the critical anionic radius of about 2·2 Å is the factor which causes the reactions of benzenediazonium salts to be of types 1 and 2 or of type 3 above. Although attention has been confined to benzenediazonium ions, the results are believed to be of general validity.

(3) *Ionic radii.*—Where available, anionic radii have been taken from Pauling [9] and cationic radii from Ahrens.[15] The following $r_{\text{eff.}}$ (in Å) have been taken from the cited reference or estimated as indicated:

N_3^-	2·04	Gray and Waddington.[16]
NMe_4^+	3·0	Yatsimirski.[8]
I_3^-	3·0	Estimated as ref. 16, from crystallographic data.[17]
$Ph{\cdot}N_2^+$	2·4	Estimated as ref. 16, from crystallographic data.[18]
$Ph{\cdot}SO_3^-$	2·55	Estimated as ref. 15, from structural data.[19] The ΔH (hydration) obtained by interpolation in Fig. 2 is in good agreement with recently reported value.[20]
CN^-	1·96	Value most consistent with crystallographic data.
BF_4^-	2·16	Estimated as ref. 7.
ClO_4^-	2·45	Cordes [21] gives 2·6 Å Yatsimirski [8] gives 2·3 Å. At high temperatures all alkali-metal perchlorates change to rock-salt structure. The average M^+ to ClO_4^- distance is 2·44 Å.

(4) *Thermochemical Data.*—All calculations in this paper are based on ΔH°_{298}(f) and ΔG°_{298}(f). These values have been taken from ref. 23, except as cited in Table 5.

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* The trends shown in Fig. 4 suggested the investigation of, and predicted the results with, *o*-toluenediazonium iodide (see above).

[15] Ahrens, *Geochim. Cosmochim. Acta*, 1952, **2**, 155.

[16] Gray and Waddington, *Proc. Roy. Soc.*, 1956, *A*, **235**, 106, 481.

[17] Tasman and Boswijk, *Acta Cryst.*, 1955, **8**, 59.

[18] Rømming, *Acta Chem. Scand.*, 1959, **13**, 1260.

[19] Sutton *et al.*, " Tables of Interatomic Distances and Configuration in Molecules and Ions," Chem. Soc. Special Publ., No. 11, London, 1958.

[20] Morris, *Tetrahedron*, 1958, **4**, 423.

[21] Cordes and Fetter, *J. Phys. Chem.*, 1958, **62**, 1340.

[22] Pritchard, *Chem. Rev.*, 1953, **52**, 529.

[23] Rossini *et al.*, Nat. Bur. Stand. Washington, Circular 500, 1952.