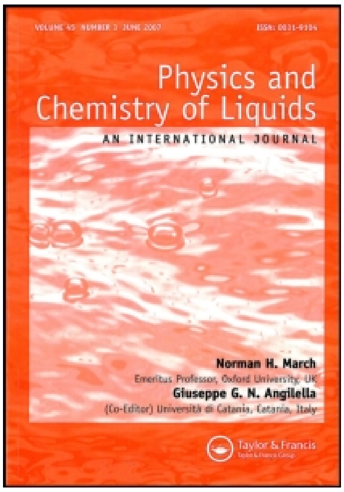

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On the Epstein-Paskin Criterion for Electrotransport in Alloys‡

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Abstract—The Epstein–Paskin criterion is examined by reference to a survey of all published data for electrotransport in alloys. The examination supports the general validity of the suggestion that ionic species of highest electron-scattering cross-section are preferentially transported to the anode and, except for transition metals, that the melting point resistivities of the liquid components provide a satisfactory parameter for the scattering cross-sections. It is suggested that the criterion is relevant to electrotransport in solid as well as liquid alloys.

The phenomenon of electrotransport, in which relative motion and hence separation of the different atomic species of an alloy is produced by the application of an electric field, has long been known experimentally.[1] It is generally considered[2,3] that the basic mechanism involves two forces: (*a*) the "field force", due to the interaction of the applied field with the charged ions, and (*b*) the "drag force", arising from the momentum exchange between the moving current carriers (electrons or holes) and the ions. However, the quantitative theory of the phenomenon remains poorly established and repeated attempts have been made to define the criteria governing the precise behaviour to be expected in any particular alloy system.

Skaupy,[4] who was the first to recognise the existence of the electron momentum exchange force, suggested (1914) that, since the field and drag forces were related to the resistivity of a metal, ions which increase the resistivity should accumulate at the anode, while those reducing the resistivity should accumulate at the cathode. Later, Kremann[5] (1926) suggested that in metallic solutions the component of lower ionization energy should accumulate at the cathode, while in 1961, after reviewing the then

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existing data, Angus, Verhoeven and Hucke[6] concluded that the alloy component with the lowest atomic weight became concentrated at the cathode. These early hypotheses, reasonable when proposed, have in turn been invalidated by subsequent experimental data.

Recently, however, a promising semi-quantitative criterion has been proposed by Epstein and Paskin.[7] Since it has become increasingly apparent that the drag force is probably the dominant factor in most electrotransport behaviour, they have suggested that, in a liquid metallic alloy, the ionic species with the highest electron scattering cross-section should be influenced to the greatest extent by momentum transfer and so preferentially transported to the anode. The degree of separation of the alloy components would be proportional to the product of electron current density, and the difference in scattering cross-section of the component ions. From the Faber and Ziman[8] model, the difference between thesc attering cross-sections will be proportional to the difference in electrical resistivities of the pure components. Thus the elements with greatest resistivity may be expected to accumulate at the anode.

Epstein and Paskin have demonstrated their resistivity criterion with experimental results for a series of solutes in liquid bismuth and mercury but clearly it is of interest to examine its validity more fully by reference to a wider variety of alloy systems. Such an examination is possible using the information obtained from a new literature survey performed as part of a recent electrotransport research project. The results of all published electrotransport studies known to the present date have been assembled; this complete detailed collection of data is available elsewhere.[9] Systems considered here are, however, confined to those where the direction of migration does not undergo reversals with increasing temperature or solute concentration. These systems, with the differences in the resistivities of their components at their melting points and the reported directions of solute migration are shown in Table 1; it should be noted that following the suggestions of Ziman[10] and Epstein,[7,11] the resistivities of the monovalent metals have been multiplied by a factor of 2.5 to compensate for the difference in structure between the monovalent and polyvalen, metals.

Examination of Table 1 reveals that, of the 98 examples listed, only nine alloy systems are in definite conflict with the Epstein–Paskin hypothesis. Five of these, Bi—Co, Bi—Ni, Sn—Mn, Fe—Ni and Ni—Fe, involve transition elements and their behaviour is readily understandable

TABLE 1 Electrotransport in liquid alloys

System	$\Delta\rho$	Solute accumulates	System	$\Delta\rho$	Solute accumulates	System	$\Delta\rho$	Solute accumulates	System	$\Delta\rho$	Solute accumulates
Na—Sr	*	N	Hg—Li	−31	C	Tl—Ag	−30	C	Sb—Ag	−71	C
—Ba	+111	A	—Cs	0	A†	—Au	+5	A	—Au	−36	C
—Ag	+19	N	—Mg	−64	C				—Zn	−77	C
—Cd	+10	A	—Ca	*	C	Ge—Al	−47	C	—Pb	−19	C
—Hg	+67	A	—Ag	−48	C	—Ga	−45	C			
									Bi—Mg	−102	C
—In	+9	A	—Au	−13	C	—As	*	A†	—U	*	A
									—Zr	*	A
—Tl	+49	A	—Zn	−54	C				—Cr	*	A
—Pb	+71	A	—Cd	−57	C	Sn—Mn	−8	A†			
			—Ga	−65	C	—Co	+54	A	—Fe	±10	C
K—Hg	+59	A	—In	−58	C	—Ni	+37	A	—Co	−27	A†
—Tl	+41	A	—Tl	−18	N	—Cu	+4	C†	—Ni	−44	A†
—Pb	+63	A	—Sn	−43	C	—Au	+30	A	—Pd	*	A
			—Pb	+4	N	—Zn	−11	C	—Cu	−77	C
Cu—H	*	C	—Bi	+38	A	—Al	−24	C	—Ag	−86	C
—Sn	−4	A†				—Ga	−22	C	—In	−96	C
			Al—H	*	C	—Tl	+25	A	—Tl	−56	C
Ag—Sn	+5	A	—Ag	+19	A	—Ge	+23	A	—Sb	−15	C
			—Au	+54	A	—Sb	+66	A	—Se	$+10^7$	A
Au—Ge	−7	C				—Bi	+81	A	—Te	+420	A
			Ga—Hg	+65	A						
Cd—Co	+68	A	—Sn	+22	A	Pb—Co	+7	A	W—Mo	*	A
—Ni	+51	A	—Bi	+103	A	—Zn	−58	C			
—Ag	+9	A				—Cd	−61	C	Fe—Mn	−84	C
—Au	+44	A	In—Co	+69	A	—Tl	−22	C	—Ni	−39	A†
—Tl	+39	A	—Ni	+52	A	—Sn	−47	C	—C	*	C
—Sn	+14	A	—Ag	+10	A	—Sb	+19	A	—S	*	C
—Bi	+95	A	—Tl	+40	A	—Bi	+34	A			
			—Sb	+81	A	—Se	$+10^7$	A	Ni—Mn	−45	C
									—Fe	+39	C†

Notes: A–B = Solvent–Solute. $\Delta\rho$ = resistivity of solute − resistivity of solvent ($\mu\Omega$ cm.)
A = anode. C = cathode. N = no effect. * = solute resistivity unavailable. † = contrary to model.

since, as Belaschenko[3] has pointed out, transition metals nay be expected to have anomalously large scattering cross-sections as a consequence of their unfilled *d*-shells. Liquid resistivity data are not available for the components in a number of systems, but for most of these cases the reported electrotransport behaviour is in accord with the anticipated relative magnitudes of the scattering factors. Thus the accumulation of U, Zr, Cr and Pd at the anode, when in Bi, is consistent with the higher scattering factors of transition elements, as mentioned above. The light elements H, C, S are invariably found to concentrate at the cathode—behaviour which can be attributed to the expected small scattering cross-section of these elements. This may indeed result in the cathode-directed field force being predominant on these solutes, in addition to preferential movement of the solvent to the anode by the momentum transfer mechanism. The failure of the Cu—Sn and Hg—Cs systems to conform to the hypothesis may be simply a reflection of the uncertainty attached to small $\Delta\rho$ values or may be due to the importance of other factors when small differences in scattering cross-section are involved.

The Epstein–Paskin hypothesis was proposed for electrotransport in liquid systems. It is possible, however, using the recently collected data, to examine its applicability to electrotransport in solid alloys. Since solid state resistivities may be complicated by zone effects and variations of lattice vibration, the melting point resistivities of the liquid components are again assumed to provide the most convenient parameter for the scattering cross-sections of the component ions. Electrotransport directions in solid alloys are compared with the corresponding $\Delta\rho$ values in Table 2. Of the 42 examples, only three behave in a manner contrary to the hypothesis. Again resistivity data are lacking in a number of cases. but in all of these the electrotransport behaviour is as would be anticipated from the foregoing discussion of the liquids. Thus H and C are once more cathode-directed while transition metals accumulate at the anode. The solid alloys provide more numerous examples of intra-transition-metal systems and consideration of the observed migration directions in these and in the various liquid alloys involving these elements suggests that the effective scattering cross-sections increase through the sequence Cr, Mn, W, Fe, (Co), Mo, Ni.

By considering the behaviour of various solutes in liquid bismuth and mercury, Epstein and Paskin have also attempted to relate the magnitude of the differential electric mobility in a liquid alloy to the solute-solvent

TABLE 2 Electrotransport in solid alloys

System	$\Delta\rho$	Solute accumulates	System	$\Delta\rho$	Solute accumulates	System	$\Delta\rho$	Solute accumulates
Cu—Fe	+72	A	Ge—Li	-11	C	Fe—H	*	C
—Co	+50	A	—Cu	-19	C	—W	*	C
—Ni	+33	A				—Mo	*	A
—Au	+26	A	Pb—Ag	-52	A†	—Cr	*	C
—Sb	+62	A	—Au	-17	A†	—Al	-100	C
						—C	*	C
Au—Pd	*	C						
			Bi—Sb	-15	C			
Zn—Ag	+6	A				Co—W	●	C
			Se—Tl	-10^7	C	—C	*	C
Al—Ag	+19	A						
—Zn	+13	A	Te—Tl	-475	C	Ni—H	*	C
						—Cr	*	C
Si—Li	-20	C						
—Cu	-28	C	Mo—Cr	*	C	—W	*	C
—Ag	-37	C	—Fe	*	C	—C	●	C
—Zn	-43	C	—Ni	●	A			
—Al	-56	C				Pd—H	*	C
—In	-47	C	W—Th	*	C			
—Bi	+49	C†	—Mo	*	A			
			—C	●	C			

Note: Symbols as for Table 1.

resistivity difference. The recent survey unfortunately has yielded only very few additional mobility data. While these are reasonably consistent with the suggestion that the differential mobility should be proportional to scattering factor differences, the quantitative transport data remain inadequate, in number and accuracy, to establish an exact correlation at this time.

It is clear, however, that the above examination of all existing electrotransport data supports the general validity of the Epstein–Paskin criterion to a remarkable degree and also now demonstrates its relevance to the solid, as well as the liquid, state. The resistivity criterion would thus appear to provide a satisfactory basis for the prediction of the qualitative electrotransport behaviour in the majority of solid and liquid alloys systems.

REFERENCES

1. Gerardin, M., *Compt. Rend.* **53,** 727 (1861).
2. Verhoeven, J. D., *Met. Revs.* **8,** 311 (1963).

3. Belaschenko, D. K., *Russian Chem. Revs.* **34**, 219 (1965).
4. Skaupy, F., *Verhandl. deut. Phys. Ges.* **16**, 156 (1914).
5. Kremann, R., *Monatsh.* **47**, 295 (1926).
6. Angus, J., Verhoeven, J. D., and Hucke, E. E., *Trans. A.I.M.E.* **7**, 447 (1959).
7. Epstein, S. G., and Paskin, A., *Phys. Letters* **24A**, 309 (1967).
8. Faber, T. E., and Ziman, J. M., *Phil. Mag.* **11**, 153 (1965).
9. Sellors, R. G. R., and Pratt, J. N., "Electrotransport in Liquid Metal Alloys"—Appendices I, II & III. Final Report (Ministry of Technology Agreement PD/27/024) (November 1968).
10. Ziman, J. M., Private communication, 1968. (Also Refs. 7 and 11.)
11. Epstein, S. G., *Advances in Physics* **16**, 325 (1967).