Fractionation of Lithium Isotopes by Crystallisation

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Fractionation of lithium isotopes has been achieved by processes like molecular destillation, electrical methods, chemical exchange, ion exchange and liquid-liquid extraction[1].

While in the case of molecular destillation, electrical methods and chemical exchange the single stage separation is of the order of several percent, in the case of ion-exchange and liquid-liquid extraction separation appears to be very much smaller.

It may be of interest therefore that by ordinary crystallisation from solutions of lithiumcompounds in water and a few organic solvents the following separation factors α have been observed by us.

Compound	Solvent	Number of samples	Temperature range in which the crystallisation occured, in °C	$\alpha = \frac{(^6\mathrm{Li}/^7\mathrm{Li})\ \text{solid}}{(^6\mathrm{Li}/^7\mathrm{Li})\ \text{solution}}$
LiCl	H_2O	2	130 → 95	1.006 ± 0.002
LiCl	H_2O	3	80 → 20	1.013 ± 0.002
LiCl	H_2O	2	0 → −70	1.018 ± 0.002
LiBr	H_2O	2	130 → 100	1.007 ± 0.002
LiBr	H_2O	2	30 → 0	1.015 ± 0.002
$LiNO_3$	H_2O	1	22 → 18	1.012 ± 0.002
Li_2SO_4	H_2O	3	0 → 95	0.999 ± 0.002
LiCl	ethanol	1	70 → 20	1.015 ± 0.002
$LiNO_3$	pyridine	1	110 → 20	0.997 ± 0.002

Table 1.

These very accurate measurements were made possible by means of a mass spectrometric technique described by Schutten[2].

The right column gives the separation factor α for an infinitesimal quantity of solid material crystallised from the bulk solution. It has been calculated with the formula for normal freezing[3]

$$\frac{c_\mathrm{S}}{c_0} = \frac{1-(1-y)^\alpha}{y} \tag{1}$$

in which c_S and c_0 are the concentrations of ^{6}Li divided by the concentrations of ^{7}Li in the solid and the original solution respectively and y is the solid fraction crystallised from the solution.

The crystallisations from the stirred* solutions took several hours. The Li salt concentrations were calculated from measurements of the volume and weight of the solutions. These determinations were done with an accuracy better than a few percent. The total error in α is almost entirely due to the mass spectrometric measurement.

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[1] Liquid-liquid extraction has been studied by S. Drury, A.E.C. report Y 785 (1951, declassified 1957). For electro-migration see A. Klemm, Int. Symp. on Isotope Separation, edit. by J. Kistemaker, J. Bigeleisen and A. O. C. Nier, North-Holland Publ. Co., Amsterdam 1958. The other methods have been studied again and a list of references of the earlier papers is given in L. Perret, L. Rozand and E. Saito, 2nd U.N. Int. Conf. on the peaceful uses of atomic energy 1958 paper A/conf. 15/P/1267.

[2] J. Schutten, Z. Naturforschg. **14 a**, 764 [1959].

[3] R. H. McFee, J. Chem. Phys. **15**, 856 [1947].

* Some experiments with LiCl in which the crystallisation took place overnight without stirring gave the same result as the ones given here.

A Three Filament Assembly for a Solid Source Mass Spectrometer with Alternately Heated Side Filaments

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For the measurement of isotopic separation factors in crystallization experiments a method has been developed to determine the ^{6}Li/^{7}Li ratio with an accuracy of about 2‰. In contrast to the conventional method[1, 2], where both side filaments are heated simultaneously, either by sending a current through them, or by the radiation from the centre filament, we apply the following method, to be used in those cases only, where sample and standard have nearly the same isotope ratio. At a side filament current zero the centre filament is heated to a temperature, where no measurable evaporation from the side filaments can be observed.

When one side filament is heated the material on it evaporates at a much higher rate than the material on the other side filament, as this one is heated by radiation only. Of course contamination occurs; in the first place, by evaporation from the "cold" filament,

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[1] M. Inghram and W. A. Chupka, Surface Ionization Source Using Multiple Filaments, Rev. Sci. Instr. **24**, 518 [1953].

[2] G. H. Palmer, Isotopic Abundance Measurement by Mass Spectrometry, Proceedings of the Conference held in the Cockcroft Hall, Harwell, 13—16 sept. 1955.