im Lösungsspektrum der Azoäther in Schwefelsäure [23] und bei anderen Azobenzolderivaten [5] an der gleichen Stelle, obwohl alle anderen Banden verschoben sind. Die Zuordnung zu dem auch bei symmetrischer Mittelgruppe nicht streng verbotenen Übergang zu $^1(\pi_1\Phi_1)^-$ bzw. zu dem Term, der bei genauerer Rechnung hieraus entsteht, ist daher wenig wahrscheinlich. Insbesondere spricht dies auch gegen eine Zuordnung zu den bei symmetrischer Mittelgruppe verbotenen Übergängen zu $^1(\pi_1\pi_2)^-$ oder zu $^1(\pi_1\Phi_2)^-$. Das Azobenzolspektrum ist demnach in Übereinstimmung mit der Struktur (II). Mit der asymmetrischen Mittelgruppe von Struktur (I) hingegen wäre es nur nach wenig wahrscheinlichen Annahmen verträglich. Aber es sind noch ergänzende Untersuchungen erforderlich, um die Entscheidung zu sichern.

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Electrolytic Separation of Deuterium; Effect of Temperature

By M. S. Raman, R. Kumar and R. L. Datta

Department of Chemical Engineering, Indian Institute of Science, Bangalore 12, India

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The effects of cathode material and temperature on the separation factor in the electrolytic enrichment of deuterium are investigated in the temperature range 30°—60 °C. Mild steel cathodes give separation factors higher than those for nickel, silver, platinum and tin, whereas an alloy of mild steel +7.85% tin gives still higher separation factors. The temperature coefficient of the separation factor ($d\alpha/dT$) for cathodes of tin and for an alloy of mild steel + tin (62.3%) is positive, whereas for other cathodes studied, $d\alpha/dT$ is negative. The temperature dependence of the separation factor is decreased by alloying mild steel with tin. It becomes zero for the alloy with 39.5% tin.

In the production of heavy water the final enrichment is often brought about by electrolysis. If electric power is very cheap, electrolysis can be employed from the very preliminary stages to the final stage of enrichment. The electrolytic cells are usually run hot, to increase power efficiency, but the separation factor decreases in general with increase of temperature. Therefore, there is an optimum value of temperature, and it would be convenient if the temperature coefficient of the separation factor could be reduced.

The effect of temperature on the separation factor has often been observed [1–7]. Although, in general, there is a lowering of the separation factor at most cathodes with rise in temperature, the anomalous behaviour of mercury and tin [6] requires further investigation.

The object of the present investigation was, therefore, to assess, in a systematic way, the effect of temperature on the electrolytic separation factor of deuterium for various cathode materials. The materials study were nickel, silver, platinum, tin, mild steel, and alloys of tin and mild steel. The range of temperatures was 30° to 60 °C. At higher temperatures losses due to evaporation are considerable, and some fractionation is taking place, in addition to corrosion of the electrodes.

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[3] D. F. Mason, R. E. Biddick and C. A. Boyd, J. Chem. Phys. **19**, 1551 [1951].
[4] J. Brun and Th. Varberg, K. Norske Vidensk. Selsk. Forh. **26**, 19 [1953].
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Experimental

The experimental set up (Fig. 1) consists of an electrolytic cell (U-tube of 18 mm inner diameter) with arrangements for circulating cold water through the jackets (length 19 cm) of the cell, for drying of hydrogen, and a hydrogen burner.

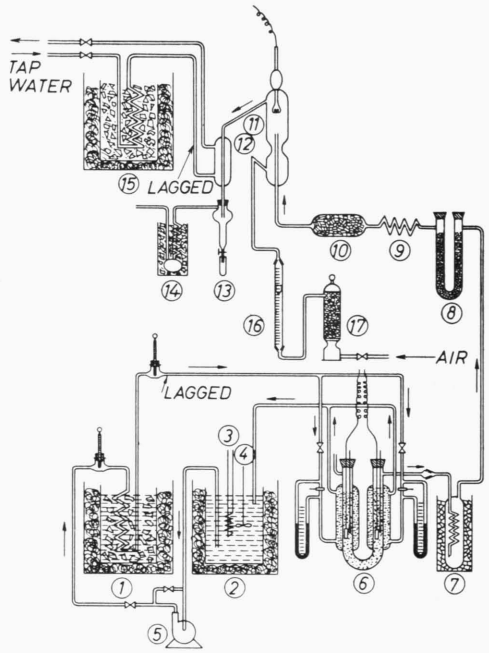

Fig. 1. Set up of apparatus for electrolysis.

1. Water cooler
2. Water reservoir
3. Immersion heater
4. Stirrer
5. Pump (circulating)
6. Electrolytic cell
7. Entrainment separator
8. $CaCl_2$ U-tube
9. Glass coil
10. Packed glass tube
11. Hydrogen burner
12. Condenser
13. & 14. Receiver
15. Water cooler
16. Rotameter
17. $CaCl_2$ tower

The electrolyte contains nearly 1.0 mole % of D_2O and 20 g of pure KOH pellets in 100 g of electrolyte. The anode is platinum. The cathodes have the form of strips (6 cm × 1 cm × 0.05 cm), polished with fine emery powder and washed well with distilled water. Thermometers with long stems dipping into the electrolyte are graduated up to 0.1 of a degree. The temperature of the electrolyte is kept constant to ±1.0 degree centigrade for a sufficient period (5 hours) by circulating cooling water through the jackets of the cell. A current of 4 A is passed through the electrolyte by applying 110 V across the terminals of the electrodes. The hydrogen evolved before being burnt in air is dried by passing through a coil immersed in an ice-salt mixture and subsequently over anhydrous calcium chloride. A glass coil and a glass bulb, packed with broken glass, are situated between the hydrogen burner and the source of hydrogen in order to prevent a flame from traveling back through the line. The water formed by combustion is condensed and allowed to drip into a receiver [13]. Any vapour escaping condensation is recovered in another receiver [14] surrounded by an ice-salt mixture.

At the end of 5 hours, electrolysis is stopped. The deuterium content of the samples is determined by the temperature float method [8]. The electrolyte left in the cell is neutralized by bubbling CO_2 through it. The sample is then purified by distillation, to remove carbonate, and then subjected to further distillation over alkaline permanganate and then over silver turnings. The material balance of the system is checked by striking a deuterium balance between the feed, the water obtained from the burner, and the unelectrolysed cell liquor. The concentration in the cell can, for subsequent runs, be calculated from the concentrations of the feed and the water from the hydrogen burner. The separation factor (α) is defined as

$$\alpha = \frac{(H/D)\,\text{gas}}{(H/D)\,\text{liq.}}$$

Discussion of Results

In order to obtain reproducible data, platinum is used as anode, because nickel gives an undesirable black precipitate, the quantity of which increases at higher current densities. A low current density (0.33 A/cm^2) is found suitable for reproducible data.

Effect of Cathode Material and Temperature on Separation Factor

Separation factors obtained for various metal cathodes at different temperatures are given in Table 1. An examination of the Table shows that mild steel gives the highest separation factors. The separation factors are found to decrease with rise of temperature for all cathodes with the exception of tin.

The Effect of Temperature on the Separation Factors of Cathodes of Alloys of Mild Steel and Tin

Cathodes made of alloys of mild steel and tin of the following compositions were investigated: (1) 7.85% tin, (2) 22.24% tin, (3) 35.05% tin and (4) 62.30% tin (weight percent). The composition of the alloys was determined by quantitative ana-

[8] E. Weingartner, R. L. Datta, R. Kumar and E. G. Mahadevan, Golden Jubilee Research Volume (Indian Institute of Science, Bangalore 12) (1959), 170.

Cathode	Temp. °C	Separation factor (α)	Mean α	Mean Deviation	$d\alpha/dT$	$d\alpha/dT$ Average
Nickel	30	5.05 4.98	5.02	$\pm$ 0.04	— 0	
	40	4.75 4.54	4.65	$\pm$ 0.10	— 0.037	— 0.033
	50	4.37 4.31	4.34	$\pm$ 0.03	— 0.031	
	60	4.17 3.90	4.04	$\pm$ 0.13	— 0.030	
Silver	30	4.71 4.81	4.76	$\pm$ 0.05		
	40	4.46 4.45	4.46	$\pm$ 0.01	— 0.030	
	50	4.29 4.19	4.24	$\pm$ 0.05	— 0.022	— 0.029
	60	3.75 3.96	3.84	$\pm$ 0.11	— 0.036	
Platinum	30	4.72 4.49	4.61	$\pm$ 0.12		
	40	4.44 4.24	4.34	$\pm$ 0.10	— 0.027	
	50	3.95 4.16	4.06	$\pm$ 0.11	— 0.028	— 0.031
	60	3.71 3.64	3.67	$\pm$ 0.03	— 0.039	
Tin	30	2,75 2.57	2.66	$\pm$ 0.09		
	40	2.80 2.99	2.90	$\pm$ 0.10	+ 0.024	
	50	3.40 3.17	3.29	$\pm$ 0.12	+ 0.039	+ 0.045
	60	4.21 3.84	4.02	$\pm$ 0.19	+ 0.073	
Mild Steel	30	6.62 6.39	6.51	$\pm$ 0.12		
	40	5.75 6.14	5.95	+ 0.20	— 0.056	
	50	5.33 5.25	5.29	+ 0.04	— 0.066	— 0.055
	60	4.95 4.75	4.85	$\pm$ 0.10	— 0.044	

Table 1. Effect of temperature on separation factor for different cathodes. Anode: Platinum. Current density: 0.33 A/cm³. Electrolyte: 0.989 mol % D_2O in 15% KOH solution. Duration of electrolysis in a single run: 5 hours.

lyses [9] for each constituent. Results with these alloys are given in Table 2. The separation factor is 7.44 for a cathode of tin alloy containing 7.85% tin (at 30 °C), a value which is higher than that of pure mild steel at 30 °C. The values at other temperatures are also found to be higher than the corresponding values for mild steel. The separation factors for the alloy with 62.3% tin are lower than those for pure tin. It is interesting to observe that the alloy with 62.3% tin behaves like tin, i. e. the separation factor increases with temperature. A comparison of the values of pure metallic cathodes and of alloys indicates that by alloying mild steel with 7.85% tin higher separation factors are obtained and that $d\alpha/dT$ is decreased from -0.055 to -0.033. By employing this alloy as the cathode, the electrolytic cell can be run hot and power can be saved [10]. On the other hand, by alloying tin with 37.03% mild steel, the separation factor is decreased and $d\alpha/dT$ is increased from $+0.045$ to 0.067.

[9] F. P. Treadwell and W. T. Hall, Analytical Chemistry, Vol. II, Chapman & Hall, London 1942.

[10] M. S. Raman, R. Kumar and R. L. Datta, Chemical Age of India, Sept-Oct. 1962.

% by weight of tin in the alloy	Temp. t °C	Mean separation factor (α)	($d\alpha/dT$)	($d\alpha/dT$) Average
	30	7.44		
	40	7.28	−0.016	
7.85	50	6.91	−0.037	−0.033
	60	6.46	−0.045	
	30	5.59		
	40	5.20	−0.039	
22.24	50	4.92	−0.028	−0.032
	60	4.64	−0.028	
	30	4.94		
	40	4.86	−0.008	
35.05	50	4.74	−0.012	−0.013
	60	4.54	−0.020	
	30	1.94		
	40	2.63	+0.069	
62.03	50	3.23	+0.060	+0.067
	60	3.93	+0.070	

Table 2. Effect of temperature on separation factor for alloys of mild steel and tin. Anode: Platinum. Current density: 0.33 A/cm². Electrolyte: 0.989 mol % D_2O in 15% KOH solution. Duration of electrolysis in a single run: 5 hours. In view of the fact that the mean deviations of separation factors varried from 0.04 to 0.2 only, in the experiments reported in Table 1, only mean values of separation factors are reported in this Table.

In Fig. 2 the experimental separation factors of Table 2 are plotted against the percentages of tin in the alloy. It is seen that the alloy containing 39.5% tin, gives a separation factor of 4.45, which is unaffected by temperature in the range 40° to 60 °C ($d\alpha/dT = 0$). For alloys containing less than 39.5% tin $d\alpha/dT$ is negative, and for those containing more than 39.5% tin $d\alpha/dT$ is positive.

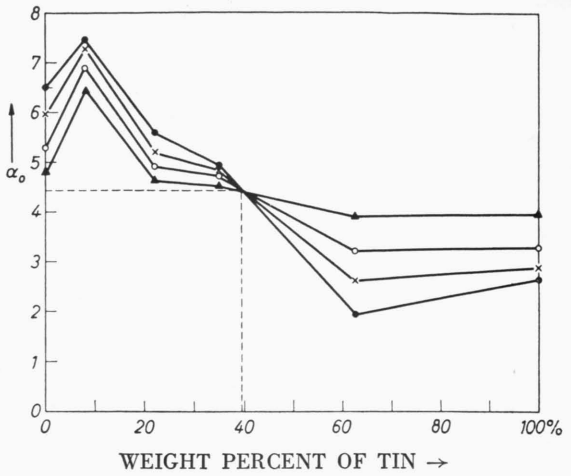

Fig. 2. Observed separation factors α_0 vs. weight percent of tin in alloys of mild steel and tin. Electrolyte: 0.989 mol % D_2O in 15% KOH solution. Current density: 0.33 A/cm². Anode: Platinum. Cathode: Alloys of mild steel and tin. ●—● 30 °C, ×—× 40 °C, ○—○ 50 °C, ▲—▲ 60 °C.

It is, of course, possible to express our results in terms of overvoltages depending on isotopic mass, temperature, and cathode material. But equilibrium separation effects should also be taken into consideration [11].

The author's sincere thanks are due to Prof. N. R. Kuloor, and to Prof. A. Klemm for their kind interest and encouragement during the progress of this work.

[11] cf. Separation of Isotopes, edited by H. London, George Newnes Limited, London 1961.