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Transient operation in thermal diffusion columns†

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Abstract. From the study of non-steady-state separation in a hot-wire thermal diffusion column, it is shown that the experimental results for the magnitude $H_0{}^2/\mu(K_c+K_d)$ are proportional to the theoretical values predicted by the Furry–Jones–Onsager (FJO) formulation.

This result, together with the earlier ones concerning the similar relations fulfilled by the logarithm of the maximum separation factor and the optimum pressure, ensures that the FJO theory is able to predict the experimental values of the three column constants H_0, K_c, and K_d, with the exception of a multiplicative temperature-independent constant, for Kr gas, in the temperature range 300–1100 K.

Our group (González-Alvarez *et al.* 1969, Hidalgo *et al.* 1970, Yarza 1970, Hidalgo 1970) have developed a new procedure for the study and treatment of the results obtained from thermal diffusion columns working in steady-state conditions. From these operations the logarithm of the maximum separation factor, $\ln \bar{Q}^*_{0\ \mathrm{exp}}$ and the pressure at which it is obtained, p^*_{exp}—known as the optimum pressure—can be determined. The results of this group show that the logarithm of the maximum separation in the steady state, as well as the optimum pressure, for various operations with the noble gases in the temperature range 300 to 1200 K, fulfill relations of the form

$$\ln \bar{Q}^*_{0\ \mathrm{exp}} = \bar{m} \ln \bar{Q}^*_{0\ \mathrm{theoret}} \qquad p^*_{\mathrm{exp}} = \bar{p}\, p^*_{\mathrm{theoret}} \tag{1}$$

when theoretical values are calculated with the help of the standard Furry–Jones–Onsager (FJO) theory (Furry *et al.* 1939, Jones and Furry 1946) and the microscopic interaction model, Lennard–Jones (12–6), which has interpolatory ability to describe the temperature variation of the gas properties in the temperature range inside the column.

We have found that the $\bar{m}$ and $\bar{p}$ constants are temperature-independent in ranges as large as those indicated above, and the precision of the fitting is often of the order of 0·5% for the standard deviation in $\bar{m}$. This fact allows the FJO theory to predict the experimental stationary column operation to within a multiplicative constant ascertainable by calibration. This fact may be useful in dealing experimentally with thermal diffusion columns.

The intention of this paper is to extend the previous results to the non-steady state.

From measurements of the separation factor Q_0 against time, the magnitude $\gamma = H_0{}^2/\mu(k_c+k_d)$ can be obtained, in which H_0, K_c and K_d (Jones 1941) are the three conventional column constants, in function of which the FJO theory describes

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the phenomenon, and the μ is the mass of gas per unit length of the column. To obtain γ from experimental data it is necessary to use an adequate formulation for the approach to equilibrium of the phenomenon. In this work the formulation proposed by Madariaga *et al.* (1970) has been used, which has been experimentally verified (Mendía 1970). This formulation contains the multicomponent nature of the isotopic mixture and takes account of the influence of the dead-end spaces in the installation.

The experimental arrangement was a hot-wire type of column. Details of the sample analysis, and the data processing have already been published elsewhere (Hidalgo *et al.* 1970, González-Alvarez *et al.* 1969). The gas employed is natural Kr and the installation is operated in total reflux. In the operations, T_1 (cold wall temperature, kept at 301 K) and T_2 (hot-wire temperature) were carefully controlled.

The experimental procedure is as follows. Once a T_2 is chosen, the gas pressure is set at the optimum pressure corresponding to T_2 and T_1. Then, at various times, samples are taken from each end of the column simultaneously. Every ln $\bar{Q}_0$, for any time, is the arithmetic mean of five runs started with the same initial conditions.

The ln Q_0 against time curve is used to calculate γ, according to the procedure outlined above. The results are shown in table 1 together with ln $\bar{Q}^*{}_{\text{exp}}$, which is needed to perform calculations.

Table 1. The reduced logarithm of the separation factor, ln $Q_{0\,\text{exp}}$, at different times

T_2 (K)	(minutes)	ln $Q_{0\text{exp}}$	γ_{exp} $\times 10^5$(s^{-1})	γ_{theoret} $\times 10^5$(s^{-1})	ln $\bar{Q}^*_{0\text{exp}}$
500	15	2·3 ±0·1			
	30	3·38 ±0·07			
	45	4·27 ±0·05			
	60	4·79 ±0·07	202 ±5	292	6·24 ±0·04
620	15	4·1 ±0·1			
	30	6·02 ±0·09			
	45	7·51 ±0·06			
	60	8·47 ±0·08	635 ±14	966	10·36 ±0·04
750	15	6·24 ±0·09			
	30	9·3 ±0·1			
	45	11·33 ±0·04			
	60	12·67 ±0·09	1476 ±25	2203	15·05 ±0·04
850	15	7·68 ±0·09			
	30	11·7 ±0·2			
	45	14·17 ±0·05			
	60	15·78 ±0·08	2338 ±94	3520	18·39 ±0·01
1000	15	9·7 ±0·1			
	30	14·76 ±0·07			
	45	18·1 ±0·1			
	60	20·03 ±0·08	3756 ±104	5989	23·58 ±0·08

γ_{exp} values have been obtained according to Madariaga *et al.* (1970) procedure. γ_{theoret} have been calculated using FJO theory and the Lennard–Jones (12–6) potential, with ϵ/k = 172·7 K. The reduced logarithm of the maximum separation factor, ln $\bar{Q}^*_{0\text{exp}}$, is needed to obtain γ_{exp}. The dead-end spaces, for the column used, are: v_e/V_{col} = 0·1 at the end and v_t/V_{col} = 0·03 at the top, V_{col} = 134·5 cm^3 being the active volume of the column.

The theoretical γ values have been calculated by means of the FJO theory and the Lennard–Jones (12–6) potential model, and the value for the interaction parameter $\epsilon/k = 172{\cdot}7$ K (Hidalgo *et al.* 1970). This value has been chosen for reasons already stated in previous papers (González-Alvarez *et al.* 1969). α_0 values have been calculated using Chapman's first approximation.

Fitting experimental γ values to theoretical ones, a new linear relation is found within the experimental error, as is shown in figure 1.

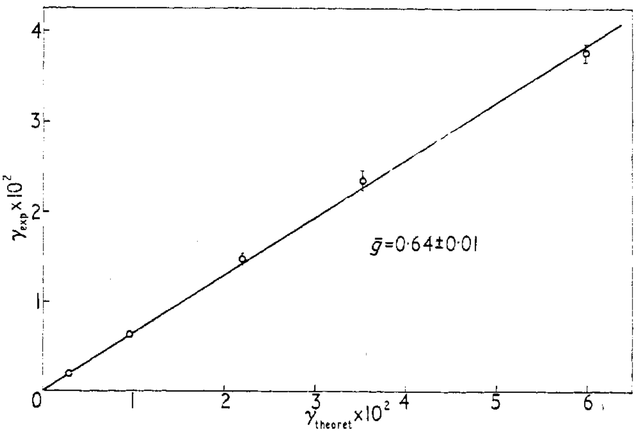

Figure 1. Experimental against theoretical values of $\gamma = H_0^2/\mu(K_c + K_d)$.

The results obtained confirm, in the first place, the excellent qualitative predictions of the FJO theory. From the proportionality of γ_{exp} against $\gamma_{theoret}$ together with those of (1), it is also deduced that the experimental values of the constants H_0, K_c, and K_d are proportional to the theoretical ones and that the proportionality constants are also temperature-independent in the range of our measurements. The existing proportionality, on the other hand, is not changed substantially by the fact that, at times, it is not easy to estimate correct values for the dead-end spaces, since Brun (private communication) has shown that the choice of slightly incorrect values of dead-end spaces changes the determination of γ_{exp} by a factor independent of the temperature. This result ensures that the linear relation of figure 1 is not changed.

More systematic experimental work with the noble gases Ar and Xe is being carried out. Since $(\alpha_0)^2$ should be relevant in γ, we are studying this fact. Also, the influence of the interaction parameters on γ is being investigated. All results are to be published.

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