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Note

On the heat of transport in thermo-osmosis

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It is shown that the heat of transport, Q^*, characterizing the energetics of the thermo-osmosis process, correlates with the quantum mechanical de Boer parameter, Λ^*.

Earlier, Lielmezs[1], has shown that the heat of transport, Q^*, of the rare gases in a rubber membrane correlates with the quantum mechanical de Boer parameter[2,3], $\Lambda^* = h/(m\varepsilon\sigma^2)^{\frac{1}{2}}$, where m, ε and σ measure the mass, potential well-depth, and collision diameter, respectively. On the other hand, the use of methods of linear thermodynamics of irreversible processes[4–6] permits to develop a general formula for the evaluation of Q^*, the heat of transport:

$$\frac{\Delta P}{\Delta T} = -\frac{Q^*}{vT} \tag{1}$$

where ΔP is a stationary pressure difference associated with a temperature difference ΔT, and v is the molar volume of the transferring fluid. Equation (1) is a general thermodynamic relation and it may be of interest to recall that it is applicable not only to the heat of transport calculation through membranes and other irreversible processes such as thermal effusion[5,6] but also to the quantum mechanical fountain effect in helium II[5–8].

The recent availability of additional heat of transport and molecular data[9,10] has made it possible to reassess the previously presented evidence[1] that heat of transport correlates with the quantum mechanical de Boer parameter Λ^*. As a matter of fact, the available data reveal (Fig. 1, Table 1) that the obtained correlation between the heat of transport, Q^*, and the de Boer parameter Λ^* is strongly monotonic and, in passing from positive Q^* to negative Q^* values, shows that for larger m (small Λ^*), the quantum corrections become vanishingly small (negative Q^*), while for small m (large Λ^*), the influence of the quantum effect on the heat of transport (positive Q^*) values is large. It appears that the so-called quantum fluids (He, H_2, Ne) all have positive heat of transport values. Clearly, the magnitude and direction of Q^* depends on the mechanism of fluid transfer through membrane at the given thermodynamic state. Yet, whether this mechanism is predominantly quantal in nature

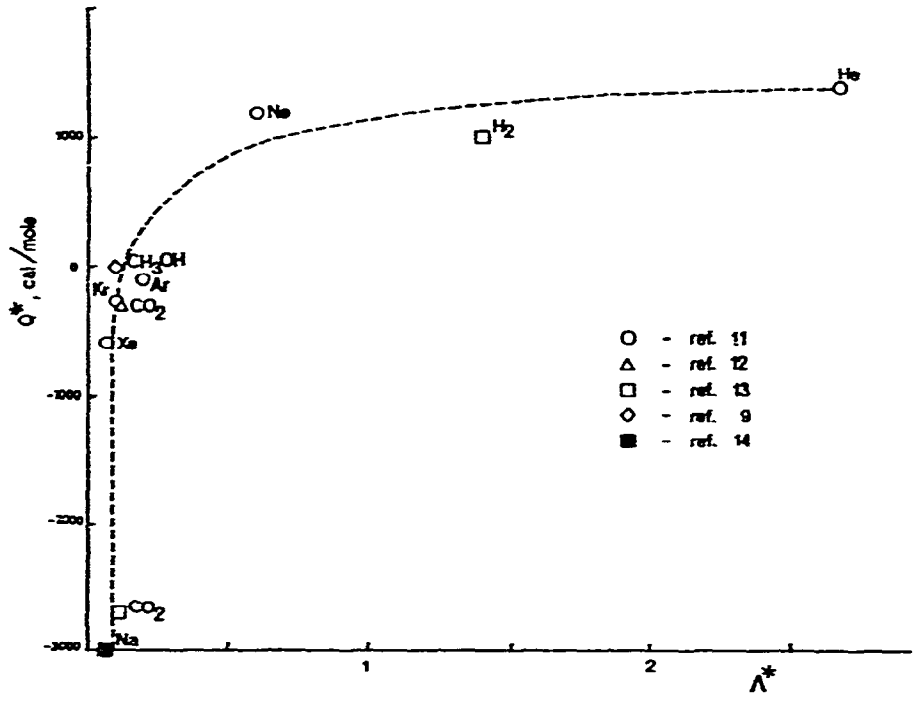

Fig. 1. Plot (compare with data found in Table 1) of the heat of transport, Q^*, versus dimensionless quantum mechanical de Boer parameter, Λ^*. Note that Q^* value ^{22}Na was obtained for solid Li-matrix.

TABLE 1

SUMMARY OF DATA

Species	$\Lambda^* = h/(m\,\varepsilon\,\sigma^2)$	*Ref.*	Q^* (*cal mol*$^{-1}$)	*Ref.*
He	2.68027	10	+1375	11
H_2	1.41009	10	+1000	13
Ne	0.60278	10	+1204	11
CO_2	0.11972	10	−308; −2700[a]	12; 13
Ar	0.20225	10	−58	11
Kr	0.09775	10	−275	11
Xe	0.06500	10	−589	11
CH_3OH	0.09862	10	−0.982[b]	9
Li	0.13367	10	−13,600[c]	15
Na	0.06896	10	−3,000[d]	14

[a] Q^* values for CO_2 appear to be very uncertain. [b] Q^* values were obtained for Cellophan (600)+ methanol system. [c] Q^* values were obtained for ^{22}Na in solid lithium-matrix. [d] Q^* values were obtained for Li^1 in liquid Li–metal matrix. This value is not shown on Fig. 1, since it is high as compared to other Q^* values obtained for fluid transfer in solid matrices (membranes). Although there is not at present sufficient evidence, part of heat effect (Q^*) may be due to the interaction between matrix and fluid in transfer.

(proposed by Fig. 1, Table 1), thus enlarging the scope of the previous thermodynamic arguments[11–13], is the subject matter of further study.

Considering the presented correlation (Fig. 1) it may well be inferred that the heat of transport, Q^*, characterizing the difference[5,6] between the mean energy, U^*, for mole transported by the migrating molecules during their passage through the barrier and the enthalpy, h^*, of the fluid in vessel from which the transfer takes place, would contain in varying amount quantum corrected energy accounting for the additional although included in Q^*, heat effect due to the thermal diffusion within the membrane. In this connection the thermo-osmotic membrane diffusion data are compared with the heat of transport value (see Fig. 1, Table 1) of thermal diffusion occurring in ionic liquids and solids[14,15]. For instance, Table 1 shows Q^* value for ^{22}Na in solid lithium matrix and Q^* value for Li^1 in liquid Li–metal matrix. This particular Q^* value is not shown in Fig. 1, since it is high as compared to other Q^* values obtained for fluid transfer in membranes. Again, although there is not at present sufficient evidence, part of heat effect (Q^*) may be due to interaction between matrix and fluid in transfer. This comparison (Fig. 1, Table 1) once more points out that the understanding of the origin of the heat of transport is not complete without considering the quantum mechanical aspects[16–19] of the transfer process.

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