

LETTER TO THE EDITOR

Non-equilibrium thermodynamics and Gorter's model of liquid helium II

Gorter's version of the two-fluid theory¹⁾ of helium II explains a great number of properties of this liquid. The author mentions that part of his results, leading to formulae for the fountain and mechano-caloric effects, could probably also be derived with the help of the Onsager relations²⁾. We found that such a calculation is actually possible and that it might throw a new light on some controversial questions.

We have considered in first instance not specially the case of helium, but an arbitrary mixture of two "isomers" 1 and 2, capable of the "chemical reaction" $1 \rightleftharpoons 2$ and enclosed in two reservoirs kept at different temperatures and connected by a capillary. The thermodynamics of irreversible processes, based on the Onsager relations, is applied to this system in which chemistry, diffusion, energy conduction and mutual effects can take place. Full details of the calculations and results for arbitrary states and chemical reaction rates will be given in an article, to be published in this journal³⁾. We will need here only the results for the case of infinitely quick reaction rate. The most important situation is the stationary state, in which the amounts of substances 1 and 2 are constant in time in both reservoirs. We then find for the equation describing both thermomolecular pressure difference and mechano-caloric effect

$$v \Delta P / \Delta T = (h - U^*) / T = \{x_1(h_1 - h_2) + h_2 - U^*\} / T \quad (1)$$

where ΔP and ΔT are corresponding pressure and temperature differences between the two reservoirs. The fractions of substances 1 and 2 are indicated by x_1 and x_2 ($x_1 + x_2 = 1$). The specific volume is $v = x_1 v_1 + x_2 v_2 = \rho^{-1}$ where v_1 and v_2 are partial specific volumes; similarly the specific enthalpy is $h = x_1 h_1 + x_2 h_2$. Application of Onsager's relations shows that U^* is the "energy of transfer" i.e. the energy transferred when one unit of mass of the mixture is transported from one reservoir to the other at uniform temperature. An alternative form of (1) is

$$v \Delta P / \Delta T = x_1(s_1 - s_2) + (h_2 - U^*) / T = x_1 \partial s / \partial x_1 + (h_2 - U^*) / T, \quad (2)$$

because at chemical equilibrium $\mu_1 = \mu_2$ (zero affinity), where μ_1 and μ_2 are the chemical potentials. The "thermal effusion" effect is under the same circumstances

$$\Delta x_1 / \Delta T = (\partial x_1 / \partial \mu_1)_{T,P} (1 - x_1) \{h_1 v_2 - h_2 v_1 + (v_1 - v_2) U^*\} / v T \quad (3)$$

These equations are derived without any particular assumption and thus valid for arbitrary "isomers". When we apply them to liquid helium II, we assume, as is usually done, that "superfluid" atoms (component 2) but no "normal" atoms (component 1) can pass through a narrow capillary. Then the heat of transfer is simply

$$U^* = u_2 + P v_2 = h_2 \quad (4)$$

and (2) is Gorter's equation

$$v \Delta P / \Delta T = x_1 \partial s / \partial x_1, \quad (5)$$

which is thus confirmed by the theory of irreversible processes. Equation (3) becomes for helium II

$$\Delta x_1 / \Delta T = (\partial x_1 / \partial \mu_1)_{T,P} (1 - x_1) v_2 (h_1 - h_2) / v T. \quad (6)$$

The foregoing calculation may be considered as a refinement of the "one fluid theory" of the thermomolecular and mechano-caloric effects by one of us ⁴).

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REFERENCES

- 1) C. J. Gorter, and J. H. Mellink, *Physica 's-Grav.* **15**, 285, 1949; C. J. Gorter, *Physica 's-Grav.* **15**, 523, 1949.
- 2) L. Onsager, *Phys. Rev.* **37**, 405, 1931; **38**, 2265, 1931; H. B. G. Casimir, *Rev. mod. Phys.* **17**, 343, 1945.
- 3) S. R. de Groot, L. Jansen and P. Mazur, *Physica 's-Grav.*, 1950.
- 4) S. R. de Groot, *Physica 's-Grav.* **13**, 555, 1947; *J. Phys. Radium* **8**, 193, 1947; *C. R. Acad. Sci. Paris* **225**, 173, 1947.