effectively at infinite temperature) combine to produce heat at an intermediate temperature (at T_0). This relation of input work to input heat through a negative efficiency is in contrast to the more usual relation of output work to input heat through a positive efficiency.

IV. SUMMARY

The proposed quantum heat engine appears to be a quantum equivalent of the well-known Carnot cycle. The efficiency expression for both is formally the same. Unlike the classical Carnot engine, however, which operates only between reservoirs at temperatures of the same sign, the quantum engine is capable of operation between reservoirs at temperatures of opposite sign. This capability would appear to make possible the calibration of negative absolute temperatures in a procedure through which one establishes a ratio of a negative to a positive temperature in much the same way that a Carnot cycle permits the evaluation of a ratio between two positive temperatures.

Ramsey[3] has shown that the description of certain classes of physical systems by a temperature variable of negative absolute value is compatible with the traditional framework of classical thermodynamics. At that time, however, no Carnot cycle or equivalent process was known which would permit the calibration of a negative temperature by determining a direct relation between a positive and a negative temperature. This gap seems to be filled by the quantum heat engine.

PHYSICAL REVIEW VOLUME 156, NUMBER 2 10 APRIL 1967

Drift Velocity and Energy of Electrons in Liquid Argon*

BRET HALPERN, JOHN LEKNER, STUART A. RICE, AND ROBERT GOMER
Departments of Chemistry and Physics and Institute for the Study of Metals, The University of Chicago, Chicago, Illinois

(Received 14 November 1966)

Measurements are reported of the energy required for injection of an electron into liquid argon and of the drift velocity of electrons in liquid argon at moderate field strength. It is found that the barrier to electron injection is −0.33 eV, in moderately good agreement with a theoretical estimate of −0.45 eV. The observed field dependence of the drift velocity is in good agreement with the recent calculations of Lekner.

THIS paper reports on measurements of the field dependence of the drift velocity and on a photoelectric determination of the binding energy of electrons injected into liquid argon. The drift-velocity measurements are an extension to lower and higher fields of the recent work of Schnyders, Rice, and Meyer.[1] The photoelectric method of determining the energy required to inject electrons into liquids has been used by Woolf and Rayfield[2] in liquid helium, but has not been applied to other systems.

The drift-velocity measurements were made by the electronic-gate method previously employed.[1] The only modification in the present experiment is the use of a glass apparatus of about 4-liter volume, containing mass-spectrometer grade argon. The argon was specified as having 3 ppm N_2, and no other detectable impurities. Further purification inside the sealed glass system was provided by a tantalum getter. A field-emission microscope incorporated into the system enabled a visual test[3] for purity to be made. The impurity level was estimated to be less than 10^{-3} ppm. Measurements were made with two drift tubes, both with a 5-mm drift space and 1-mm spacing between grids. The grids were 85% transmission nickel electromesh spot-welded to stainless-steel rings of 12-mm i.d. Electrons were produced in the liquid by field emission from tungsten tips. Currents of 10^{-13} to 10^{-11} A were obtained at the collector, that is, after passing through five grids. The results obtained with the two drift tubes are compared with previous data and with theory in Fig. 1. The theoretical line is derived from the solution of the Boltzmann equation in the single-scatterer approximation,[4] as described in Ref. 5. We see that nonohmic behavior does indeed set in at fields of about 200 V/cm, as predicted.[4] The dashed line gives the drift velocity in the ohmic region, corrected for multiple scattering (energy renormalization and effective mass) following Wigner and Seitz and Bardeen, taken from Ref. 5.

The photoelectric measurements were made with a similar glass system, again with mass-spectrometer grade argon and tantalum getter. The cathode and

* Supported in part by the Directorate of Chemical Sciences, U. S. Air Force Office of Scientific Research.

[1] H. Schnyders, S. A. Rice, and L. Meyer, Phys. Rev. Letters **15**, 187 (1965); H. Schnyders, S. A. Rice, and L. Meyer, Phys. Rev. **150**, 127 (1966).

[2] M. A. Woolf and G. W. Rayfield, Phys. Rev. Letters **15**, 235 (1965). We are grateful to J. Jortner for bringing this paper to our attention.

[3] B. Halpern and R. Gomer, J. Chem. Phys. **43**, 1069 (1965).

[4] J. Lekner and M. H. Cohen, Phys. Rev. (to be published).

[5] J. Lekner, Phys. Rev. (to be published).

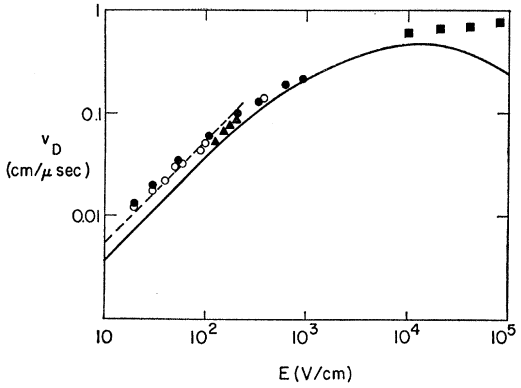

FIG. 1. Field dependence of the drift velocity of electrons in liquid argon. Squares—data of D. W. Swan [Proc. Phys. Soc. (London) **83**, 659 (1964)]; triangles—data from Ref. 1, taken at 85°K; circles—present work, obtained at 85°K with two cells. The line is the single-scatterer theory taken from Ref. 5, and the dashed line is the same corrected for multiple scattering in the Ohmic region.

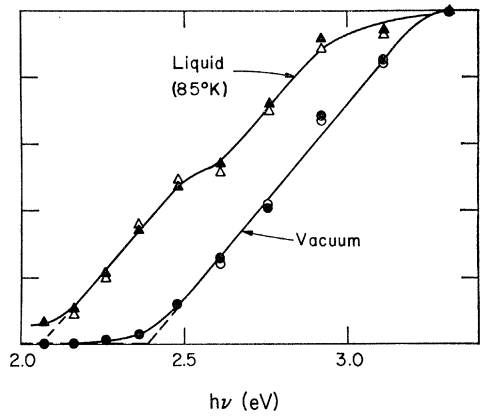

FIG. 2. Photoemission yields in vacuum and in liquid, per unit light intensity. The extrapolated curves meet the energy axis at 2.39 and 2.06 eV. Each set of points is the average of three runs. The origin of the kink in the liquid curve between 2.5 and 2.6 eV is not known; it is reproducible and persists when a tungsten-filament lamp is used as light source.

anode were platinum disks, the photocathode having a layer of barium deposited on it in vacuo. The Ba layer was deposited by heating a notched ironclad barium wire hairpin (Kemet getter wire). The photoelectric current, measured with a vibrating-reed electrometer, was determined as a function of wavelength. The light source used was a high-pressure xenon arc lamp. The intensity of light passing through a grating monochromator and a $\frac{1}{4}$-in. slab of glass was measured with a CsBr-window thermocouple. The energy required to inject an electron into the liquid is found from the energy displacement of the photoemission yields shown in Fig. 2. The vacuum yield is obtained by condensing the argon in an arm of the glass system with liquid hydrogen. This reduces the pressure in the system to about 10^{-13} Hg. The collecting field between photocathode and anode was about 200 V/cm in both the liquid and vacuum runs. The peak currents in vacuum and liquid were, respectively, of order 10^{-10} and 10^{-11} A. The energy difference between the liquid and vacuum photoemission yield curves is -0.33 eV, with an uncertainty of about -0.05 eV. The finding by Mignolet[6] that adsorption of Xe does not change the work function of K or Ca surfaces strongly suggests that changes in work function arising from specific adsorption effects can be ignored. It is interesting that field emission through multilayers of Ar yields a work-function decrease of 0.60 eV from the vacuum value of 3.77 eV [7] (actually tungsten plus monolayer of Ar). This higher value could be a result of the lower temperature (20°K) and the high field (3×10^7 V/cm), both of which will tend to increase the density of the Ar, relative to that of the field-free liquid near its boiling point. The energy predicted by the simplest multiple-scattering theory, namely the Wigner-Seitz boundary condition that the electron s wave have zero gradient on the Wigner-Seitz sphere, is calculated, in Ref. 5, to be -0.46 eV.

We are grateful to Professor David Beaglehole for experimental advice.

[6] J. C. P. Mignolet, J. Chem. Phys. **21**, 1298 (1953).
[7] R. Gomer, Australian J. Phys. **13**, 391 (1960).