

A CALCULATION OF INTERNAL KINETIC ENERGY AND POLARIZABILITY OF COMPRESSED ARGON FROM THE STATISTICAL ATOM MODEL

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Synopsis

From Jensen's and Gombás' modification of the statistical Thomas-Fermi atom model, a theory for compressed atoms is developed by changing the boundary conditions. Internal kinetic energy and polarizability of argon are calculated as functions of pressure. At 1000 atm. an internal kinetic energy of about 5.2 kcal/mole is found; the polarizability is about 2.9% less than that at zero pressure. The change with pressure of these quantities is in rough agreement with experimental results at high densities.

§ 1. *Introduction.* Total energy, internal kinetic energy and polarizability have been calculated as functions of pressure for models of compressed atomic hydrogen^{1) 2) 3)} and helium⁴⁾, *viz.*, atoms enclosed in a spherical box. In these calculations rigorous wave functions were used for atomic hydrogen³⁾ and a very good approximation (from variation theory) for helium⁴⁾.

Since experimental values of internal kinetic energy⁵⁾ and polarizability^{6) 7)} of compressed argon are now available, it was thought of importance to try to find theoretical values for this atom. The statistical atom model, in particular Jensen's and Gombás' modification^{8) 9)} of Gombás' (G, § 11) generalized Thomas-Fermi model, seemed an appropriate starting point for these calculations. (The original Thomas-Fermi model is less satisfactory, since it gives infinite values for the polarizability of free atoms). In § 2 we give an outline of the way in which the Jensen-Gombás method can be adapted to a statistical model of the compressed argon atom. In § 3

and § 4 the internal kinetic energy and the polarizability are calculated as functions of pressure. The results are compared with the experimental values.

§ 2. *Statistical model for compressed argon.* For the free atom there exists in the statistical model a sphere with radius r_0 , outside of which the electron density ρ vanishes. In that case the pressure of the electron gas is zero at the spherical boundary at r_0 .

As a model of compressed argon we take the statistical model with a value of r_0 smaller than that for the free atom. At the sphere with radius r_0 the electron gas has then a pressure P_0 , which is different from zero, and which is supposed to be balanced by the external pressure.

In the theory of Jensen-Gombás for the free atom there is a condition which follows from the vanishing of P_0 at r_0 . In our case of the compressed atom this condition has to be replaced by one which pertains to a non-vanishing P_0 . For the free atom a certain reduced electric potential $\varphi(r)$ corresponds to zero pressure P_0 at radius r_0 . Now for the compressed atom we take a different function φ , which belongs to a different value of r_0 and to a corresponding $P_0 \neq 0$.

In the actual calculation the different function φ quoted above is obtained by changing the parameter k of (G 10.10) from reference ⁹). Then r_0 (or the corresponding reduced x_0 of G. p. 94) and $\varphi(x_0)$ follow from (G. 10.9). (Furthermore the electron density ρ , especially $\rho_0 \equiv \rho(x_0)$, can be derived from (G 7.19)). Finally P_0 , which is equal to $-(1/4\pi r_0^2)(dE/dr_0)$ (E is the energy), is calculated from (G. 11.12). This formula does not quite fit in the Jensen-Gombás modification, but rather in Gombás' generalized Thomas-Fermi model (G, § 11). However, also Jensen uses this formula in his theory for the free atom (compare G, p. 93. We also, with Gombás, use in (G 11.12) always the λ_0 calculated for the free atom; *i.e.*, we use the simplification of the generalized Thomas-Fermi model given in G, p. 99 ff.).

TABLE I

Quantity Unit	k 10^{-6}	x_0 —	r_0 a_0	P_0 $e^2 a_0^{-4}$	P_0 atm.	$\cdot 10^3$ kcal/mole	α \AA^3	$\alpha \alpha_f$ —
	6.0416	11.10	3.895	0	0	0	2.9604	1
	6.06	11.10	3.895	3.0 10^{-8}	8.70	.048	2.9596	.9997
	7	11.05	3.878	1.574 10^{-6}	457	2.48	2.921	.937
	8	10.99	3.857	3.347 10^{-5}	972	5.09	2.878	.972
	12	10.80	3.790	1.1324 10^{-3}	3287	15.34	2.733	.923

In table I the corresponding values of k , x_0 , r_0 and P_0 are given, the latter both in atomic units $e^2 a_0^{-4} \equiv e^{10} m^2 \hbar^{-8}$ and in atmospheres.

§ 3. *The internal kinetic energy.* The kinetic energy of the electron is (G 3.1)

$$E_k = \alpha_k \int \varrho^{5/3} dv. \quad (1)$$

With (G 7.11) and (G 7.19) this gives

$$E_k = B \int_0^{x_0} \varphi^{5/2} x^{-1/2} dx = 2B \int_0^{x_0} \varphi^{5/2} d\sqrt{x}, \quad (2)$$

where $2B$ is a constant ($2B = 1.35541 e^2 a_0^{-1} Z^{7/3} N^{1/3} (N-1)^{-1/3}$, with $Z =$ atomic number, $N =$ number of electrons) which for argon has the value 7.3604_5 kcal/mole. From (2) and the functions φ of § 2, the

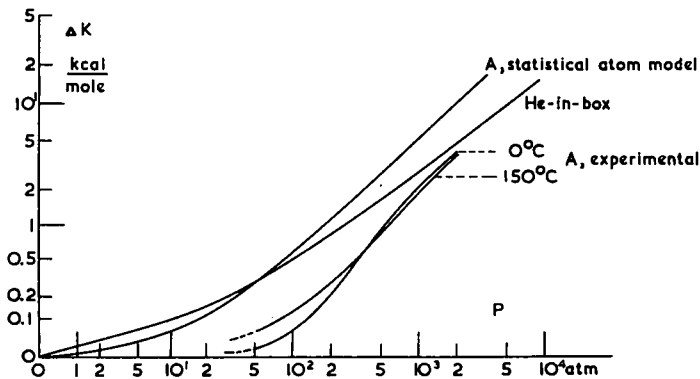


Fig. 1. Change of internal kinetic energy of argon by compression.

kinetic energy E_k can be calculated. The change ΔK of E_k by compression is an important physical quantity which can be calculated from experimental compressibility data⁵). We obtain it by calculating the difference of E_k and the corresponding quantity E_{kf} for the free atom:

$$\Delta K = E_k - E_{kf} = 2B \left\{ \int_0^{x_0} (\varphi^{5/2} - \varphi_f^{5/2}) d\sqrt{x} - \int_{x_f}^{x_0} \varphi_f^{5/2} d\sqrt{x} \right\}. \quad (3)$$

Here the index f indicates quantities of the free atom. The results of the calculation are given in table I and fig. 1. In this figure are also given experimental values for argon and, for comparison, theoretical results for compressed helium with the model of the atom enclosed in a spherical box⁴). The scales for ΔK and P are pseudo-logarithmic, i.e., linear in $\log(\Delta K + 1)$ and $\log(P + 1)$, respectively. Only

at high pressures is the trend of the experimental and theoretical curves comparable. This is understandable since the model describes essentially repulsion at high densities but ignores attractive forces.

§ 4. *The polarizability.* We use the formula (G. 28.7) for the electric polarizability, which is valid for the Jensen-Gombás modification of the statistical model:

$$\alpha = K^2(r_0) / \{ 2 \int_0^{r_0} K(r) e^{1/3}(r) dr + (5\kappa_k / 6\pi e^2) K(r_0) \}, \quad (4)$$

with

$$K(r) = \int_0^r e^{1/3}(s) s^4 ds. \quad (5)$$

Using (G 7.11) and (G 7.19) we write (4) for argon as follows:

$$\alpha = 3.39144 \cdot 10^{-3} \chi^2(x_0) / \{ \chi(x_0) + 1.05882\omega(x_0) \}, \quad (6)$$

with

$$\chi(x) = \int_0^x \varphi^{1/2}(y) y^{7/2} dy, \quad (7)$$

and with

$$\omega(x) = \int_0^x \chi(y) \varphi^{1/2}(y) y^{1/2} dy, \quad (8)$$

where α is in cubic Ångstrom units. We have calculated α from (6) with the help of φ from § 2. The results are given in table I and fig. 2. In fig. 2 the calculated quantity α/α_f , where α_f is the polarizability

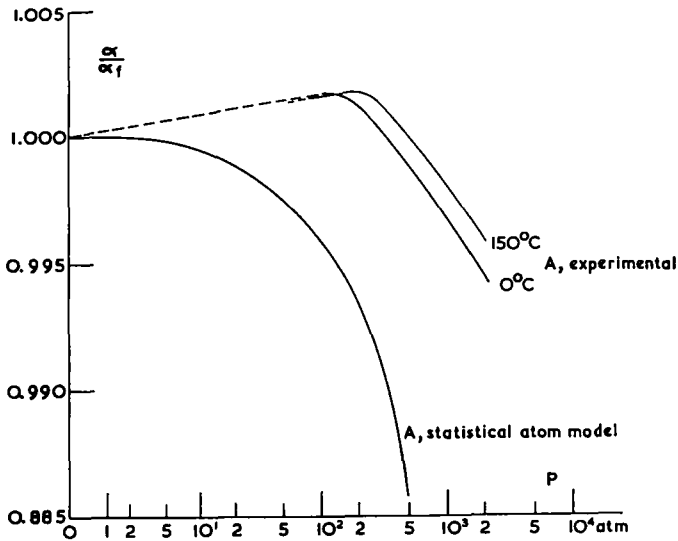


Fig. 2. The polarizability of the compressed argon atom.

of the free atom, is plotted as a function of the pressure P_0 . The experimental values of α/α_0 have been calculated from the measured dielectric constants ⁶⁾ by means of Kirkwood's statistical theory ⁷⁾. Just as in § 3, only the change with pressure at high densities is well explained by the theory.

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ERRATUM

In fig. 2, p. 913, for "0°C" read "25°C"; for "150°C" read "125°C".

REFERENCES

- 1) Michels, A., de Boer, J., and Bijl, A., *Physica* **4** (1937) 981.
- 2) Sommerfeld, A. and Welker, H., *Ann. Physik* [5] **32** (1938) 56.
- 3) de Groot, S. R. and ten Seldam, C. A., *Physica* **12** (1946) 669.
- 4) ten Seldam, C. A. and de Groot, S. R., *Physica* (in the press).
- 5) Michels, A., Lunbeck, R. J. and Wolkers, G. J., *Appl. sci. Res.* **A 2** (1951) 345.
- 6) Michels, A., ten Seldam, C. A. and Overdijk, S. D. J., *Physica* **17** (1951) 781.
- 7) de Boer, J., van der Maesen, F. and ten Seldam, C. A., *Physica* (in the press).
- 8) Jensen, H., *Z. Phys.* **101** (1936) 141.
- 9) Gombás, P., *Die statistische Theorie des Atoms und ihre Anwendungen*; Wien, Springer, 1949. We shall refer to equations, sections, etc. of this book as G, followed by the number of the item concerned.