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The Thermodynamic Properties of Helium Gas

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The Joule-Thomson coefficients of the preceding article and the *pv* data of Holborn and Otto are here used to calculate the most important thermodynamic properties of helium. The *variation of the specific heat with pressure* is small. The computed values of the *specific volumes* compare excellently with those from the data of Holborn and Otto. Simple relationships are shown to exist between *the coefficient of free expansion* η *and the intrinsic energy variation* λ. Convenient equations are derived for computing these coefficients. η is independent of the pressure and λ is proportional to the square of the pressure except at the lowest temperatures. Both η and λ are zero at about $-70°C$, are positive below this temperature and are negative above. Their numerical value above $-70°C$ is everywhere small. The pressure and temperature behavior of η and λ is explained by a kinetic theory taking into account the change in the total potential energy stored by collision between the helium atoms when the pressure is altered. The law of force between two helium atoms, consistent with this theory, is of the type giving rise to the same mutual potential energy of two helium atoms as deduced from considerations of the quantum theory. It is extremely doubtful that the trend of η at high temperature leads ultimately to the perfect gas state.

THE isenthalpic curves for helium between -190 and $+300°C$ over the pressure range 1 to 200 atm. have been given in a preceding article.[1] These experimental curves are straight lines over this temperature-pressure range except at the lowest temperatures. The slope of these lines, μ, called the porous plug coefficient, has also been given with some discussion of its significance.

As in the similar work with air,[2, 3] this coefficient may be combined with specific heat and *pv* data to yield, often with high precision, a variety of thermodynamic properties. Among these the free-expansion coefficient, $\eta \equiv (dT/dp)_u$, previously quite unknown, is of great interest as giving direct experimental information about the dependence of the law of force between molecules upon both pressure and temperature. This is of immediate application in the atomic structure studies. The variation of intrinsic energy with volume at constant temperature, $\lambda \equiv (du/dv)_T$, raises some interesting questions by its negative sign.

SPECIFIC HEAT C_p

The specific heat of helium has been measured by several workers. The best determinations are those by Scheel and Heuse.[4] They give

t	$-180°C$	$18°C$
C_p	1.237	1.251

in calories per gram degree. These are the only available data on the variation of C_p with temperature.

The meagerness of this knowledge of C_p as a function of temperature prevents the spreading of the values over the pressure range as in the air work.[2] The most that can be done is to tabulate a factor which may be used to spread C_p over the pressure range when it becomes known over a temperature range.

Thus in Fig. 1, the isenthalps h_1 and h_2 are straight lines of slope μ_1 and μ_2. One can therefore

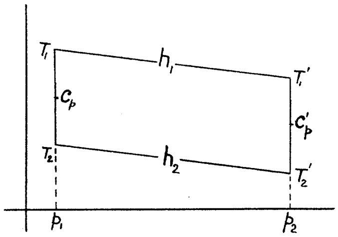

FIG. 1.

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[1] Roebuck and Osterberg, Phys. Rev. **43**, 60 (1933).

[2] Roebuck, Proc. Am. Acad. **60**, 537 (1925).

[3] Roebuck, Proc. Am. Acad. **64**, 287 (1930).

[4] Scheel and Heuse, Ann. d. Physik [4] **37**, 79 (1912).

write

$$T_1=T_1'+\mu_1(p_1-p_2),$$

$$T_2=T_2'+\mu_2(p_1-p_2)$$

or

$$T_1-T_2=(T_1'-T_2')+(\mu_1-\mu_2)(p_1-p_2).$$

If C_p and C_p' are the average specific heats over the range indicated, then

$$\frac{C_p}{C_p'}=\frac{T_1'-T_2'}{T_1-T_2}=1-\frac{\mu_1-\mu_2}{T_1-T_2}(p_1-p_2)$$

$$=1+M(p_2-p_1), \qquad (1)$$

where C_p' is the specific heat at the higher pressure. M is a function of the temperature but not of the pressure. From the data of the previous article,[1] M has been calculated and is given in Table I.

Table I. *Values of M.*

t°C	$M\times10^5$ (atm.)$^{-1}$	t°C	$M\times10^5$ (atm.)$^{-1}$	t°C	$M\times10^5$ (atm.)$^{-1}$
275	−6.2	125	+1.2	− 25	3.0
225	−2.4	75	1.6	− 75	4.2
175	−0.6	25	2.2	−125	13.2

This means, for example, that the difference between the C_p at 1 and at 200 atm. at 275°C is about 1 percent. This difference in C_p decreases to zero at 160°C and to −1 percent at −100°C. The following calculations cover the range 1 to 40 atm. and −50 to 150°C. The pressure variation of C_p in this range is less than 0.1 percent.

The temperature range variation as measured by Scheel and Heuse[4] is 1.2 percent between 18 and −180°C. This variation, although it may be proportionately less between −50 and 150°C, handicaps seriously much of the following calculations and introduces uncertainty into some of the conclusions.

Coefficient of Volume Expansion, α_p

The equation[3]

$$\alpha_p\equiv(1/v)(dv/dT)_p=(1/T)[\mu C_p/v+1]$$

was used to compute α_p. C_p was taken as constant. (See Table II.)

At the low pressure end of the range $\mu C_p/v$ is between 0.0009 and 0.0005 and if μ, C_p, and v are each known to 1 percent, α_p is relatively correct to one part in 10^5. At the high pressure end of the range $\mu C_p/v$ lies between 0.025 and 0.013 so that here α_p is relatively correct to about a part in 10^4. If only relative values are desired, these figures are probably better than any directly determined values. They are also excellent in the absolute sense, since this absolute value depends finally on the average coefficient 0–100°C which is undoubtedly the most carefully measured of any volume-temperature coefficient of helium.

Table II. $\alpha_p\times10^3$ *in* °C^{-1}.

$p(m)$	p(atm.)	−50°C	0°C	50°C	100°C	200°C
1	1.31579	4.47738	3.65834	3.09260	2.67842	2.11256
5	6.57895	4.46183	3.64777	3.08485	2.67254	2.10887
10	13.1579	4.44253	3.63464	3.07521	2.66522	2.10427
20	26.3158	4.40448	3.60865	3.05612	2.65069	2.09511
30	39.4737	4.36714	3.58302	3.03723	2.63630	2.08602

Specific Volume

In Fig. 7 of the earlier paper[1] that part of the curve between −50 and +150°C is almost a straight line, so that

$$\mu=\mu_0+a(T-T_0)$$

where $a=-2.12\times10^{-5}$ atm.$^{-1}$; $\mu_0=-5.98\times10^{-2}$ °C/atm.; $T_0=273.15$°K. The fundamental equation for the porous plug effect,

$$\mu C_p=T(dv/dT)_p-v, \qquad \text{(Eq. (2), p. 296)}^4$$

may be written

$$\frac{\mu C_p}{T^2}=\left(\frac{d(v/T)}{dT}\right)_p=\frac{C_p}{T^2}[\mu_0+a(T-T_0)]$$

where T falls between -50 and 150°C. Upon integrating,

$$\frac{v}{T}-\frac{v_0}{T_0}=C_p(\mu_0-aT_0)\left(\frac{1}{T_0}-\frac{1}{T}\right)+aC_p\log_e\frac{T}{T_0}\equiv E,\quad(2)$$

which will hold for any one constant pressure.

Since v/T varies slowly along an isopiestic, E is a small correction term. This equation has been used to calculate v over the temperature range at each of a set of pressures from the above values of a, μ_0, T_0 and values of v_0/T_0 properly chosen from the data of Holborn and Otto.[5] In this calculation C_p was obtained from a linear extrapolation of the values of C_p given by Scheel and Heuse.[4] The values of v are given in Table III, where they are paired with values taken from Holborn and Otto's work. The uncertainty of 10–20 percent in the slope a is the major source of error in these calculations. But the error introduced in the value of E by this uncertainty is less than 3 percent. Since the error in the selected values of C_p should be less than 1 percent, an error of 4 percent in E in the temperature range -50 to 150°C is an overestimate. Values for v at 200°C are also given in Table III. The error in E at this temperature is less than one percent greater than in the values of E for the range -50 to 150°C. The relative value of E and v_0/T_0 for the various pressures in Table III is such that the above errors in E introduce uncertainty of 2 in the sixth significant figure of the 1 meter row, the fifth of the 10 meter row, and the fourth of the 20, 30, and 40 meter rows. Since the errors estimated above are the maximum, this method of calculation is an excellent one for obtaining the temperature variation of the specific volume at constant pressure, and may be used to give more reliable values for this temperature variation than the directly measured values.

TABLE III. *Specific volume, v, in liters/gram. Holborn and Otto's data in italics.*

$p(m)$	-50°C	0°C	50°C	100°C	200°C
1	3.48045 *3.48063* −18	4.25962	5.03875 *5.03871* +4	5.81789 *5.81780* +9	7.37612 *7.37580* +32
10	0.350707 *0.350755* −48	0.428604	0.506483 *0.506512* −29	0.584360 *0.584378* −18	0.740078 *0.740067* +11
20	0.176851 *0.176879* −28	0.215792	0.254719 *0.254725* −6	0.293638 *0.293616* +22	0.371445 *0.371418* +27
30	0.118888 *0.118924* −36	0.144842	0.170782 *0.170797* −15	0.196714 *0.196710* +4	0.248546 *0.248534* +12
40	0.0899141 *0.0899503* −36.2	0.109376	0.128823 *0.128821* +2	0.148264 *0.148256* +8	0.187112 *0.187091* +21

A comparison of the calculated values of v with those taken directly from the tables of experimental data of Holborn and Otto[5] shows excellent agreement. The slight deviations indicate no systematic error in the pressure variation and possibly a small systematic error in the temperature variation. These deviations are in most cases larger than our estimated maximum error and should therefore be interpreted as error in their data.

COEFFICIENT OF FREE EXPANSION, $\eta\equiv(dT/dp)_u$

For the first calculation of η the equation[3]

$$\eta[C_p-(d(pv)/dT)_p]=\mu C_p+(d(pv)/dp)_T$$

was used. C_p is again assumed constant as 1.251 cal./g °C. Since $(d(pv)/dT)_p=(pv)\cdot\alpha_p$, this was readily obtained from Holborn and Otto's data[5] and α_p from Table II. The data for $(d(pv)/dT)_p$ show a maximum variation over this range of temperature and pressure of only 0.7 percent. They are effectively constant over the pressure range. The term, $(d(pv)/dp)_T$, comes directly from Holborn and Otto's data under suitable modification of the units. The data show that this term varies only slightly over this temperature range and almost imperceptibly over the pressure range. μ and C_p are both independent of the pressure. Hence η is nearly independent of the pressure but varies with the temperature. The values of η so obtained are listed in Table IV.

TABLE IV. $\eta[=(dT/dp)_u]$ *in °C/atm.*

t°C	-50	0	50	100	200
$-\eta\times10^3$	1.71	3.92	7.30	11.3	14.3

It will be observed that in the temperature range of Table IV, η is negative, is very small, is

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[5] Holborn and Otto, Zeits. f. Physik **30**, 320 (1924).

TABLE V. γ *in atm.*$^{-1}$.

$p(m)$	$-50°$C	$0°$C	$50°$C	$100°$C	$200°$C	p^{-1}(atm.)
1	0.759345	0.759471	0.759558	0.759629	0.759724	0.76
5	.151352	.151472	.151545	.151628	.151712	.152
10	.0753545	.0754743	.0755589	.0756292	.0757135	.076
20	.0373604	.0374779	.0375616	.0376308	.0377145	.038
30	.0246996	.0248149	.0248975	.0249660	.0250489	.02533

independent of the pressure and increases numerically with rising temperature. The negative sign was entirely unexpected, since it means that helium becomes warmer on free expansion, and led to a careful check on these calculations. The possibility of a gas warming on free expansion is excluded in current texts on heat and kinetic theory which in the light of these data require revision.

ELASTIC COEFFICIENT, γ

The equation[3] (page 313)

$$-\gamma \equiv \frac{1}{v}\left(\frac{dv}{dp}\right)_T = \eta\left[\frac{41.38\ C_p}{pv} - \alpha_p\right] - \frac{T\cdot\alpha_p}{p}$$

has been used to calculate γ. (See Table V.) Since the values are obtained from measured small differences, they are of high precision, which is however difficult to determine. Hence an ample number of figures are given without any claim to an accuracy extending to the last figure. The reciprocals of the pressures are given in the last column to the right. γ is everywhere less than $1/p$, the value for an ideal gas, and approaches it more closely at the higher temperatures and lower pressures. Helium is thus uniformly less compressible than the ideal gas which it resembles in this respect more closely at these temperatures and pressures.

INTRINSIC ENERGY VARIATION WITH VOLUME, λ

$$\lambda \equiv (du/dv)_T = T\cdot\alpha_p/\gamma - p.$$

This equation[3] (page 315) was used to calculate λ. The values are given in Table VI. They are all very small and negative. This means that the intrinsic energy store at any fixed temperature decreases as the volume increases.

Table VII shows that λ is sharply proportional to p^2. This has been predicted from van der Waals equation by using $\lambda = a/v^2$ and substituting for v from $pv = RT$. Eq. (6) also shows that $\lambda : p^2$ since $(dp/dV)_T : p^2$.

TABLE VI. $-\lambda\times 10^2$ *in atm.*

$p(m)$	$-50°$C	$0°$C	$50°$C	$100°$C	$200°$C
1	0.0021	0.0036	0.0056	0.0078	0.0077
5	.052	.091	.090	.191	.194
10	.21	.37	.49	.79	.79
20	.83	1.51	2.34	3.13	3.15
30	1.85	3.36	5.28	7.07	7.08

TABLE VII. $-\lambda/p^2\times 10^5$ *in (atm.)*$^{-1}$.

$p(m)$	$-50°$C	$0°$C	$50°$C	$100°$C	$200°$C
1	1.16	2.19	3.46	4.62	4.62
5	1.22	2.14	3.31	4.51	4.51
10	1.16	2.19	3.41	4.62	4.62
20	1.11	2.18	3.44	4.62	4.62
30	1.11	2.18	3.44	4.63	4.62
Average	1.15	2.18	3.41	4.60	4.59

η AND λ, SECOND METHOD

A plot of λ/p^2 against temperature from Table VII and of η against temperature from Table IV, showed that both λ and η go to zero at about $-70°$C. This suggested immediately that λ and η may be more simply related than indicated by the complex equations used for their calculation. Moreover, simpler methods for these calculations greatly facilitate the estimation of the effect of experimental error.

Let $\eta' \equiv (dT/dv)_u$ and C_v be the specific heat at constant volume.

$$\eta' = -(du/dv)_T(du/dT)_v^{-1} = -\lambda/C_v$$

since

$$(du/dT)_v = (dq/dT)_v \equiv C_v.$$

Also

$$\eta' = -(dT/dp)_u(dp/dv)_u = \eta(dp/dv)_u;$$

$$\therefore\quad \eta = -(\lambda/C_v)(dv/dp)_u = -(\lambda/pC_v) \times[C_p\eta - T(dv/dT)_p]. \quad (3)$$

(See second paper[3] on air, p. 296, Eq. (1).)

$$\eta = \lambda T(dv/dT)_p[pC_v + \lambda C_p]^{-1}.$$

λC_p is small as compared to pC_v even at low pressures, so that with good approximation

$$\eta=(\lambda T/pC_v)(dv/dT)_p[1-K\lambda/p],\ K\equiv C_p/C_v. \quad (4)$$

Neglecting the small correction term, $K\lambda/p$, and obtaining $(dv/dT)_p$ from the equation for helium,[5] $pv=RT+bp$,

$$\eta=\lambda RT/p^2C_v \quad \text{or} \quad \lambda T/p^2\eta=\text{const.} \quad (5)$$

This is in good agreement with the results in the last column of Table VIII. Eq. (5) expresses the temperature dependence of λ when the temperature dependence of η is known.

TABLE VIII. *Relation between η and λ.*

t°C	T°K	$-\eta\times10^3$	$-\lambda p^{-2}\cdot10^5$	$\lambda p^{-2}T\eta^{-1}$
−50	223.15	1.78	1.15	1.44
0	273.15	3.92	2.18	1.52
50	323.15	7.30	3.41	1.51
100	373.15	11.3	4.60	1.52
200	473.15	14.4	4.59	1.51

An examination of Eqs. (3), (4) or (5) shows that $\eta=0$ when $\lambda=0$, $p\neq0$, so that the curves of Fig. 2 should drop to zero at the same temperature. The experimental data, the kinetic theory discussed below and the thermodynamic relations indicate that η does not go to zero at zero pressure. On the other hand, these indicate that λ does become zero at zero pressure. This is not inconsistent with Eq. (3) above, since, for example, $(dp/dv)_u$ is approximately equal to $(dp/dv)_T$ which goes to zero at zero pressure.

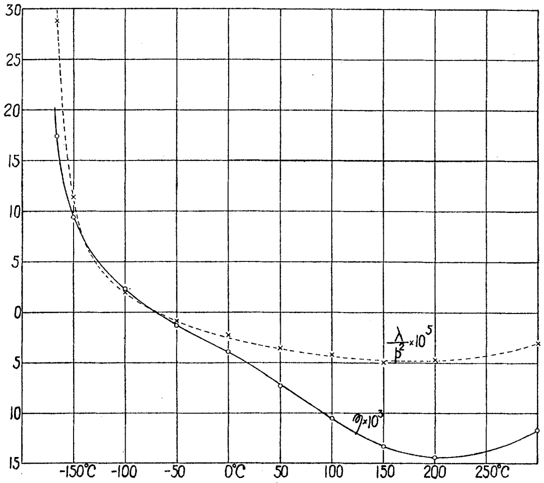

FIG. 2. η and λ/p^2 as functions of temperature.

These equations, as do other thermodynamic equations, show that η', as the definition of the coefficient of free expansion, would have led to simpler expressions than η. Also, it appears that λ is a more fundamental thermodynamic quantity than either η or η'.

It can be shown that

$$(dh/dp)_T=-\mu C_p$$

where $h\equiv u+pv$, the enthalpy. Hence,

$$\begin{aligned}-\mu C_p&=(du/dp)_T+(dpv/dp)_T\\&=\lambda(dv/dp)_T+(dpv/dp)_T.\end{aligned}$$

$$\therefore\quad \lambda=-(dp/dv)_T[\mu C_p+(dpv/dp)_T]. \quad (6)$$

When the experimental data used in the previous calculations for λ were substituted into Eq. (6), values identical with the previous results were obtained for λ. The terms μC_p and $b=(dpv/dp)_T$ (Table IX) are opposite in sign in the temperature range of these calculations and differ only a few percent in magnitude so that a small proportionate error in either of these terms introduces a larger proportionate error in λ. A plot of the b values given by Holborn and Otto[5] against temperature shows that the point at 100°C falls above the curve by more than one-half percent. The irregularities of this curve and the variation of C_p with temperature are the major sources of error in the preceding calculations leading to Tables IV and VII.

In Table IX the values of λ/p^2 in column 7 have been computed from Eq. (6) using the smoothed values of b, and, for the region below −49°C, using values of C_p obtained by assuming a linear variation with temperature between the 18° and −180°C values given by Scheel and Heuse.[4] The difference between columns 6 and 7 at −50°C results from the different value of C_p used, while at 100°C the difference arises from the different value of b used. The values in column 7 are the more reliable.

λ/p^2 must ultimately decrease numerically with rising temperature, since in Eq. (6) $(dp/dv)_T : 1/T$. This decrease is already apparent in Fig. 2. However, consideration of the manner in which μC_p enters Eq. (6) shows that the probable rise of C_p with temperature would retard this decrease. At temperatures below −50°C, λ/p^2 begins to show pressure dependence,

TABLE IX. *Summary of η and λ.*

1 t°C	2 b H.&O.[5] cal./g atm.	3 b W.G.H.[6] cal./g atm.	4 $-\mu C_p$ cal./g atm.	5 b smoothed cal./g atm.	6 $(+\lambda/p^2)10^5$ Table VII	7 $(+\lambda/p^2)10^5$ Eq. (6)	8 $+\eta\times 10^3$ Eq. (5)
300	0.06342		0.07231	0.06365		−3.05	−11.7
200	.06685	0.06474	.07769	.06676	−4.59	−4.66	−14.4
150			.07806	.06822		−4.69	−13.3
100	.06877	.06832	.07731	.06956	−4.60	−4.19	−10.5
50	.07092	.06913	.07644	.07073	−3.41	−3.56	− 7.30
0	.07159	.07066	.07456	.07157	−2.18	−2.21	− 3.91
− 50	.07207		.07331	.07209	−1.15	−0.86	− 1.29
−100	.07192		.07023			1.97	2.29
−150	.06891		.06195			11.4	9.41
−183	.06295		.05010			28.8	17.4

since for these low temperatures both μC_p and b vary with the pressure. For this reason λ/p^2 has been calculated in this region for one atmosphere.

λ will later be used to calculate the Kelvin temperature of the ice point from the constant volume helium thermometer readings. In this connection an estimate of the error in λ is desirable. This error is about 20 percent at 0°C and 12 percent at 100°C, or about 15 percent over the 0 to 100°C range.

The values of η given in column 8 are calculated from λ/p^2 in column 7 by means of Eq. (5). The three low temperature values are consequently for one atmosphere. These values agree with those in Table IV obtained by a quite different method of calculation, except for the −50°C and 100°C points already discussed in connection with λ/p^2. This latter group of values of η are probably the more reliable.

Columns 7 and 8 of Table IX have been used to plot the curves of Fig. 2. As previously pointed out, these curves must go through zero at the same temperature (−70°C), above which helium warms on free expansion. It is to be noted that there is a factor of 100 between the scales. In the temperature range of Fig. 2 the curves are similar in trend. At temperatures above those in the figure both η and λ/p^2 appear to be going toward zero again. By combining Eqs. (5) and (6) one obtains

$$\eta = \text{const.}\ (\mu\cdot C_p + b). \qquad (7)$$

The percentage error in η is therefore very nearly equal to that in λ (see discussion following Eq. (6)). As discussed, this error is considerably larger than that in b and μC_p since b and μC_p are nearly equal numerically. Within the temperature range of Table IX both b and μC_p rise to a maximum and appear to be decreasing at approximately the same rate at the highest temperatures. Since this decrease is slow (6 percent in 100°C), Eq. (7) indicates that from these experimental data alone η will decrease slowly with increasing temperature. The probable increase in C_p with temperature should partially offset this decrease. It is, however, uncertain whether or not η is decreasing at the highest temperature since the error in η is here about 10 percent. This analysis of pv and porous plug data then suggests that at the highest temperature the curve for η will depart from the horizontal more slowly than in Fig. 2.

A comparison of Eqs. (6) and (7) shows that since $(dp/dv)_T : 1/T$, the curve for λ/p^2 should go toward zero faster than that for η by the factor $1/T$.

APPLICATION TO KINETIC THEORY

It will be shown here, as a direct deduction from the preceding experimental data, that the behavior of helium on free expansion is determined by the changes which occur in the total potential energy of collision of the mass of atoms when free expansion takes place. The general form of the deduced law of force is of the type deduced elsewhere[7] from considerations of the quantum theory.

Kinetic theory explanations of the large cooling of a gas on free (Joule) expansion as, for example, with air, have necessarily to be based

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[6] Wiebe, Gaddy and Heins, J. Am. Chem. Soc. **53**, 1721 (1931).

[7] Penney, Phys. Rev. **42**, 585 (1932).

on the presence of attractive forces against which work is done at the expense of the store of kinetic energy. The free expansion coefficient for air is a marked function of the volume and hence these forces cannot be negligible at distances of the order of the mean free path.

Since helium warms on free expansion, one thinks first of the possibility of these forces being repulsive. For helium the value of η is independent of the pressure. That is, at any one temperature,

$$\eta \equiv (dT/dp)_u = K_1.$$

If C_p is also constant,

$$C_p \cdot \Delta T = K_2 \cdot \Delta p = F \cdot \Delta x.$$

Hence for a fixed Δp the energy involved is a constant independent of the pressure. F is the repulsive force and Δx is the change in the average separation due to the Δp and in which it is assumed that the work done by F over Δx supplies the $(C_p \cdot \Delta T)$ energy. Noting that $\Delta v = K_3 x^2 \cdot \Delta x$ and $pv = \text{const.}$ one finds that $F : x^{-4}$. This result is not in agreement with similar expressions resulting from measurements on viscosity[8] and from considerations of the quantum theory,[7] which lead to higher negative powers.

Moreover, the data above show that η decreases and changes sign with falling temperature, while remaining independent of the pressure and therefore of the volume, for the major part of the range. This requires these forces to be a function of the velocity of the molecules even to the changing of sign. The assumption of this type of repulsive force is thus quite untenable.

Dr. R. Rollefson of our laboratory suggested that the collision energy in the gas may need to be taken into account. During a collision the colliding molecules decrease their kinetic energy by the amount necessary to supply the required work against the repulsive forces. This provides a means by which the energy of the gas may be shifted between potential and kinetic forms by variation of the collision velocity and of the number of collisions in progress at any instant. As will presently appear, the assumption of repulsive forces extending over a small part of the mean free path permits a qualitative explanation of the observed behavior of η for helium and avoids as well the impass discussed in the preceding paragraphs.

In the simple kinetic theory where the molecules are treated as highly elastic spheres with hard sharp boundaries, the time of collision is made extremely short. While the maximum energy store per collision is the same, the number of collisions in progress at any instant is made small enough that for the purpose in hand the potential energy involved may be neglected.

Since there are no forces acting between the helium molecules at their average separation, change of this separation does not involve work and there will be no free expansion effect from this cause. The number, z, of collisions in progress at any instant in a fixed mass of gas at a given temperature is proportional to the density and hence to the pressure, since Boyle's law holds to a good approximation. Therefore $\Delta z/\Delta p = K$, a constant. If ϵ is the average potential energy of a collision, then $\epsilon\Delta z$ is the change in potential energy. In a free expansion at a fixed initial temperature, with a given pressure drop, Δp,

$$\epsilon\Delta z = K\epsilon \cdot \Delta p.$$

Where only repulsive forces are present, $\epsilon\Delta z$ is a decrease in the potential energy which appears in the kinetic form by an amount $C_v \cdot \Delta T$, where ΔT is the observed rise in temperature. Then

$$-\epsilon \cdot \Delta z = -K\epsilon \cdot \Delta p = C_v \Delta T.$$

$$\therefore \quad (\Delta T/\Delta p)_u \equiv \eta = -K\epsilon/C_v.$$

Hence in such a free expansion ΔT is proportional to Δp since for helium C_v and ϵ are constant and Boyle's law is obeyed. Thus η should be independent of the pressure and be of negative sign. This is in agreement with the experimental data of Table IV.

The above argument relating to the independence of η on the pressure can be expected to hold only if the average molecular separation, even at the highest pressures, exceeds greatly the range of the repulsive force.

The number of collisions in progress at any instant and the character of these collisions are both functions of the temperature. The number of collisions per molecule at a fixed volume will to a first approximation be proportional to the

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[8] Lennard-Jones, Proc. Roy. Soc. **A107**, 157 (1925).

average velocity of the molecules, that is, proportional to the square root of the Kelvin temperature. On this account η would become larger numerically with rising temperature.

The number of collisions at any instant at any temperature will depend also on the duration of the individual collision as a function of the temperature. It is not evident, without a general solution of the collisions as a two body problem, whether the above function increases or decreases with the temperature.

In general, the average potential energy per collision, ϵ, is an increasing function of the temperature since the depth of penetration is increased at higher molecular velocities. For the special case of the head-on collision in which both colliding molecules come to rest, the potential energy increases as the absolute temperature.

These considerations would lead one to expect that η should increase in absolute value more rapidly than the first power of the absolute temperature. Consideration of the data for η, Table IV, shows that it is very approximately proportional to $(T-163)^{1.33}$ for temperatures above -50°C.

The values of η from Tables VII and IX are plotted against temperature in Fig. 2. The curve crosses the zero axis at -70°C and rises rapidly thereafter. This corresponds with the observed behavior of air[3] for which η decreases rapidly with rising temperature, passing, undoubtedly, through zero at a somewhat higher temperature.

If there be added to the repulsive force field about the molecule an attractive field decreasing much less rapidly with distance, then as a pair of molecules approach each other they pass first through an attractive force field, with increasing velocity, and into the repulsive field where their approach is stopped. For high speeds of approach the loss in potential energy in the attractive field is relatively small, and the time spent there is also small, so that the contribution to the total instantaneous energy of collision is small. But as the molecular speed is reduced the depth of penetration for glancing collisions will increase on the average, thus increasing the contribution of those collisions which do not approach near enough for the repulsive field to act, and at the same time increasing the average time spent in the attractive field. Thus as the molecular speed is reduced, the subtraction of the attractive field from the potential energy of collision at any instant increases both from the increasing energy of the glancing collision and from the longer time spent in the attractive field. Simultaneously, the contribution of the repulsive field is falling due to the fall in molecular velocity. Thus the collision energy decreases more rapidly than the temperature. Evidently $-C_v\cdot\eta$, the ratio of the collision energy change to the pressure change, will move rapidly toward zero with falling temperature and finally become positive.

As this condition is approaching, η must become a function of the pressure, and its temperature dependence become still more complicated, since finally all the molecules are continually in the state of collision, that is, continually within the range of each other's force field.

The mutual potential energy between two helium atoms as a function of their distance of separation has been calculated from the quantum theory. The results are summarized by W. G. Penney[7] and have been used by Kirkwood and Keyes[9] as the foundation of an equation of state from which they calculate with considerable success a number of properties of helium. This mutual potential energy appears as the sum of two terms, both of which drop off rapidly with atomic separation but much the more rapidly for the positive term due to the force of repulsion. The repulsive force field thus forms a core surrounded by an attractive force field. This is obviously in agreement with that postulated above to explain the behavior of η.

The above collision hypothesis predicts the pressure behavior of λ as appears from the following argument. If z represents the number of collisions in a given mass of gas at any instant, it has been shown above that at constant temperature $z : p$. Hence, where ϵ is the average energy per collision,

$$(\epsilon dz/dp)_T = \text{const.} = (du/dv)_T(dv/dp)_T = -\lambda v/p = -\lambda K/p^2$$

since Boyle's law is closely obeyed by helium. Hence $\lambda : p^2$ on this collision hypothesis. This agrees with the data of Table VII.

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[9] Kirkwood and Keyes, Phys. Rev. **37**, 832 (1931).

Perfect Gas Theory

A perfect gas is usually defined as one for which $(pv)_T=\text{const.}$ and $\eta=0$. The experimental observations that Boyle's law holds exactly at sufficiently low pressure and, that Boyle's law holds better at higher temperatures, have led to the conclusion that any gas becomes a perfect gas at sufficiently low pressures and high temperatures. The above conditions are satisfied most nearly by helium.

When μ and η are calculated from (pv) and specific heat data alone, they appear as small differences between much larger experimental quantities. The magnitudes and trends of these small differences prove to be too unreliable for testing the departure of helium from the condition $\eta=0$. Direct experimental measurements on either μ or η have not been available. As a result, statements regarding the manner in which a real gas approaches ideality have been based entirely upon its pv behavior.

The above data for helium show that η is independent of pressure to the extent that μC_p and b are also. Above 0°C the latter are experimentally independent of the pressure in the range 1–40 atmospheres. Since there are no obvious reasons for supposing that this pressure independence should not continue indefinitely below one atmosphere, it appears that, contrary to the usual conclusion from its pv behavior, helium does not become a perfect gas at low pressure.

Neither the data nor the preceding kinetic theory gives any clear support to the hope that, on the other hand, η will go to zero at some still higher temperature and thus satisfy the conditions for ideality. This appears from the above analysis of the data for η. Thus the departure of the curve for η, Fig. 2, from horizontality is first very slow and, second, somewhat open to question. Further, granting that the upward trend of the curve is actual, it must approach the axis asymptotically in order to satisfy the ideality demand. In the latter event, the temperature at which η can become vanishingly small is very high. The kinetic theory discussed earlier in this paper predicts the pressure behavior quantitatively, and the prediction is in excellent accord with the observations. The theory predicts the temperature behavior qualitatively, and is in general agreement with the observations. There is no factor in this theory which tends to diminish the numerical value of η above 0°C. On the contrary, the theory shows that η should continue to increase numerically with increasing temperature.

In conclusion, there appears to be an experimentally measurable limit in the approximation of helium to a prefect gas state at any pressure or temperature.

The helium used in these experiments was supplied by the Bureau of Mines of the United States Government. We regret that by oversight this statement was omitted from the first paper on helium.[1] Their cooperation in the matter made this experimental work possible, and we have appreciated it very greatly.

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In a following article, the data on μ and λ will be used to calculate the value of the ice point on the Kelvin scale from the available gas thermometer data.