LOW TEMPERATURE PHYSICS

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PREFACE

The properties of matter at extremely low temperatures interest the physical scientist because under these conditions molecular motion decreases in amplitude and quantum laws are manifested in characteristic fashion. This book is an account of such properties. At low temperature the quantum-theory description of the properties of matter should be in close accord with experimentation. Often this is so, and the discrepancies between theory and experimental results may be removed by refinement or closer approximations. But just as often there are exciting surprises, and this is especially true of superfluid helium and of superconductivity. Much of the theory of these physical phenomena is in a controversial state. The properties of helium gas and hydrogen gas show quantum effects at low temperatures, and these matters are extensively discussed herein. The complex magnetic and electric permeability of matter at low temperatures affords important current fields for research. The thermal energy in the solid state at low temperatures obeys quantum laws, and thermal energy measurements indicate a number of interesting examples of such characteristic behavior.

The direct aim of the course in which this book was developed has been the stimulation of research in low-temperature physics, both experimental and theoretical. A feature of the course was that every third meeting included the presentation by a student of an important paper from the research literature. This not only broadened the range of topics, but stimulated valuable discussion of those selected. It also had a valuable "feed-back" effect on the subsequent choice of subject matter and helped greatly to crystallize the organization of this book. It seemed worth while to measure the success of the text material by the extent to which it furnished a basis for comprehension and constructive discussion of important current research papers in the low-temperature field.

The author acknowledges the creative effort and reporting of low-temperature physics data and theory by many scientists from all nations. William V. Houston, President of The Rice Institute, has given generously of his time in reviewing and consulting on many topics of the book.

The author wishes to express his appreciation also for the careful attention and criticism provided by Dr. John R. Pellam of the National Bureau of Standards, and by Professor Kurt A. G. Mendelssohn, F.R.S., of Oxford University. During 1952–1953 the author lectured this material at The Sorbonne, and he acknowledges this privilege with the warmest thanks to the Faculty of Science, University of Paris, for their generous invitation. The considerable task of the actual preparation of manuscript was made pleasant through the use of "Tall Timbers," for which the author thanks Dr. and Mrs. J. Bryan Eby. The author is most grateful for the unfailing confidence and encouragement shown by Jane Hafner Squire.

<div align="right">Charles F. Squire</div>

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CHAPTER 1

GAS LIQUEFACTION AND THE EQUATION OF STATE

It has been well over one hundred years since the first liquefaction of gases took place by means of simple compression and some seventy years since scientists began to understand that cooling with compression could liquefy a further group of gases. The early research by Cailletet, Andrews, and Claude opened up the field of the study of thermodynamic equilibrium between the gas, liquid, and solid states. By the year 1900 several low-temperature laboratories existed, notably at Krakow in Poland and at Leiden in Holland. By then the entire problem of liquefying gases was well understood so that the era of commercial gases was opened. The invention of the Dewar flask, of heat insulation by glass wool, and the development of suitable compressors are but a few of the engineering aspects which have led to the ease of attaining low temperature. There are now many laboratories in nearly every country in the world in which the production of many liters of liquid helium is regarded as rather commonplace and as simply one of many research tools used to study the properties of matter. The Claude process of cooling by an adiabatic expansion engine has had the most spectacular success. With the clever developments by Peter Kapitza and by Samuel Collins the expansion engine has become the most widely used device for producing liquid helium. These expansion engines are not the whole story of the production of liquid helium, and we shall see that the Linde process was used by Kamerlingh Onnes in Leiden and that an expansion bomb has been widely used by F. E. Simon at Oxford. In this first chapter we shall discuss the Claude process and the Linde process.

Equation of State for a Gas

We must review the thermal properties of ordinary gases. In Fig. 1.1 the well-known plot of pressure against volume for a series of isothermals is reproduced for a standard substance such as nitrogen and serves to illustrate the existence of an equation of state. The functional relation between volume, pressure, and temperature is simple for the gas at relatively high temperatures and becomes more complicated at temperatures approaching possible liquefaction. The curves for constant temperature in Fig. 1.1 show the following important experimental facts:

1. At temperatures above the T_c curve, isothermal compression does

1

not lead to formation of a coexistent liquid phase. In such high-temperature regions the simple kinetic theory of atoms moving rapidly about leads to the equation $PV = nRT$, where P is the pressure in atmospheres, V the volume in liters, n the number of moles of the gas, R the gas constant in units of energy per mole degree, and T the absolute temperature.

2. Compression along the critical isotherm leads to complete liquefaction at the critical point without change of volume. There is no latent heat of vaporization at the critical point.

3. Temperatures below T_c are characterized by a region in which the gas may be liquefied by compression, during which the pressure remains constant. The further the temperature is lowered below the critical temperature, the smaller is the pressure needed for liquefaction. The region between all liquid and all gas is marked by dotted curves.

The equation of state is not simple for the gas phase whose temperature is near or below the critical temperature T_c. The best representation may be given by a power series expansion due to Kamerlingh Onnes:
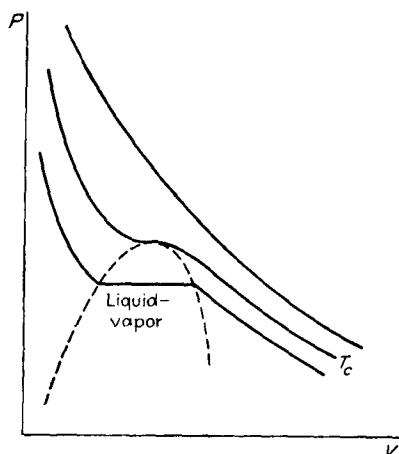
FIG. 1.1. Pressure plotted against volume for an arbitrary gas.

$$PV = nRT \left(1 + \frac{nB}{V} + \frac{n^2C}{V^2} + \cdots \right) \tag{1.1}$$

In this equation of state the new quantities B and C are called the second and third *virial* coefficients, and their values may be taken from experimental isotherms. The derivation of the virial coefficients from atomic theory constitutes the material to be treated in Chap. 3. The word *virial* was used by Professor R. Clausius in discussing gas kinetic theory.[1] Clausius' virial theorem implied the existence of forces between molecules, and the word virial was carried over by Onnes to give the coefficients a descriptive meaning.

An earlier form of the equation of state was given by van der Waals:

$$\left[P + a \left(\frac{n}{V} \right)^2 \right] [V - nb] = nRT \tag{1.2}$$

[1] R. Clausius, *Ann. Phys. u. Chem.*, **141**, 3, 1870; *Compt. rend.*, **70**, 1314, 1870.

where the new constants introduced are a and b. The constant a has the effect of altering the pressure exerted on the volume walls due to attraction forces between the atoms. The constant b accounts for the volume occupied by the atoms themselves in the space. Table 1.1 gives some values of these van der Waals constants for a few gases. It will be noted that the fourth column of the table, giving the volume per mole of the liquid, shows a smaller value than the constant b for all gases except helium. Here is the first clue to an important low-temperature physics problem, *i.e.*, the large volume occupied by liquid helium.

TABLE 1.1. VALUES OF THE VAN DER WAALS CONSTANTS FOR SOME GASES

Gas	a, dyne cm^4/mole^2	b, cm^3/mole	V/n, liquid phase
A	1.27×10^{12}	36	
O_2	1.49×10^{12}	32.2	25.7
N_2	1.36	38.3	32.8
Ne	0.207	24.0	
H_2	0.25	26.5	26.4
He	0.035	23.6	27.4
CO_2	3.64	42.5	41.7
H_2O	5.53	30.4	18.0

The van der Waals equation is not accurately valid, but it is a useful equation to discuss because it brings out many fundamental characteristics which guide our thinking about the production of low temperatures. Suppose we consider the van der Waals equation for the critical temperature T_c and solve for the pressure

$$P = \frac{nRT_c}{V - nb} - \frac{n^2 a}{V^2} \tag{1.3}$$

We may set the first two derivatives of P by V equal to zero at the critical point because the plot of P against V shows an inflection point.

$$\left(\frac{\partial P_c}{\partial V}\right)_T = 0; \qquad \left(\frac{\partial^2 P_c}{\partial V^2}\right)_T = 0$$

These equations allow us to solve for the critical values

$$P_c = \frac{a}{27b^2}; \qquad V_c = 3nb; \qquad RT_c = \frac{8a}{27b}$$

In Table 1.2 are given the critical temperature and pressure for a number of gases. A little study of the magnitude of the values shows at once that the constant a in the van der Waals equation plays the most important role with respect to the temperatures required to liquefy any gas. A small constant a means going to very low temperatures to pro-

duce the liquid.   An interesting relationship called the *law of correspond-ing states* may be obtained if we simply express the pressure, volume, and temperature in the van der Waals equation in units of their critical values.

$$\left[\frac{P}{P_c} + \frac{3}{(V/V_c)^2}\right]\left[\frac{V}{V_c} - \frac{1}{3}\right] = \frac{8T}{3T_c} \tag{1.4}$$

Reducing all gases to one equation of state allows us to see at a glance for any given gas whether the temperature and pressure existing within the working volume are to be considered high or low for that substance. Thus, room temperature would be considered a very high temperature

TABLE 1.2.   EXPERIMENTAL CRITICAL TEMPERATURE AND PRESSURE VALUES

Gas	T_c, °K	P_c, atm
CO_2	304.2	73.00
Xe	289.8	58.22
Kr	209.4	54.24
A	150.7	48.00
O_2	154.0	49.7
N_2	126.0	33.49
Ne	44.8	26.88
H_2	33.2	12.8
He	5.25	2.26

for nitrogen because the ratio 290:126 is much larger than 1.   Yet room temperature is comparatively low for Xe and very low for water.   We shall seek justification for the law of corresponding states in Chap. 3.

Entropy and Enthalpy

It will be useful to remind the reader of the thermodynamic concepts of entropy and enthalpy of a system.   The entropy S in units of energy per degree absolute temperature T is identified with the Clausius theorem concerning any reversible cycle.   During the reversible process, the system may absorb an increment of heat đQ, and the entropy change is

$$dS = \frac{đQ}{T} \tag{1.5}$$

If the inexact differential đQ can be expressed by the thermodynamic variables, we may divide by T and integrate the expression to obtain the entropy of the system.   This formulation of the second law leads one to examine the entropy increase in all naturally occurring processes. One must deduce that the entropy of a system is a measure of the degree of disorder existing in the system because in all naturally occurring proc-

esses entropy and disorder increase together. As is well known, statistical mechanics then formulates the entropy of a system from this concept.[1]

A useful thermodynamic potential is the enthalpy H of a system such as a gas:

$$H = U + PV \tag{1.6}$$

The internal energy U of the system is defined through its differential:

$$dU = đQ - P\,dV \tag{1.7}$$

In the discussion which follows we shall use these broad definitions of entropy and of enthalpy. Later on we shall need the thermodynamic potentials $A = U - TS$ and $G = H - TS$; these are the Helmholtz potential and Gibbs potential, respectively.[2]

Production of Low Temperatures with Gases

Claude Expander. Now let us return to the problem of producing low temperatures by means of gas liquefaction with the combined arrange-
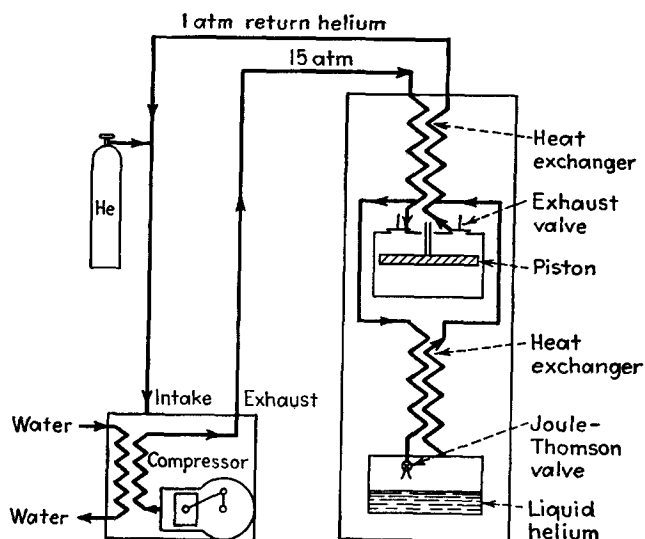
Fɪɢ. 1.2. Flow diagram of helium liquefier.

ment of a Claude expansion engine and a Joule-Thomson expansion valve. Figure 1.2 gives the scheme of the process. Gas is compressed mechanically, and by water cooling the heat developed during the work is removed. The gas then enters the liquefier where it immediately begins to be cooled with the cold gas which has been through the liquefier ahead of it. How that gas became cold we shall presently describe.

[1] J. C. Slater, "Introduction to Chemical Physics," New York, McGraw-Hill, 1939.

[2] M. Zemansky, "Heat and Thermodynamics," 2d ed., New York, McGraw-Hill, 1943.

From the heat exchanger, the gas enters the expansion chamber when-
ever the inlet valve is opened.   The inlet valve closes quickly, and the
gas continues to expand, doing work on the piston.   This work is mechan-
ically absorbed by means of a drive-rod and crankshaft arrangement.
These operations are easily followed on a pressure-against-volume plot in
Fig. 1.3.   They are marked *a* for valve open, *b* for valve shut, and the
point *c* is the bottom of the cylinder stroke.   At this point the exhaust
valve opens to allow the gas to be pushed out of the expansion chamber.
Finally the exhaust valve is closed at point *d*, and the cycle is ready to
repeat with the next charge of gas from the high-pressure line.   All of
this is very elementary, but now let us see how this has produced a drop
in temperature.   The expansion has taken place at nearly constant
entropy, and neglecting frictional effects, we may simply state that the
drop in temperature of the gas is required to offset the drop in pressure
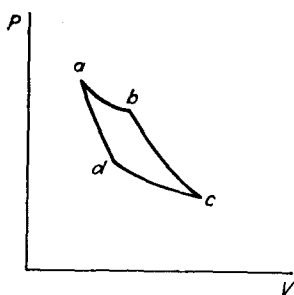which took place in the expander.

FIG. 1.3.   Pressure-vs.-volume diagram
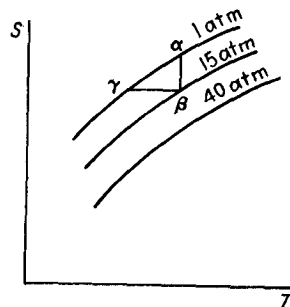showing expansion–engine cycle.

FIG. 1.4. Entropy-vs.-temperature dia-
gram showing isothermal compression
and constant-entropy expansion.

Entropy Changes and Temperature Drop.   These concepts are basic to
our understanding of the production of low temperatures.   The physical
meaning of entropy as a measure of the degree of disorder in the system
helps us to visualize the process.   The entropy-against-temperature plot
in Fig. 1.4 shows a series of constant-pressure curves.   At any given tem-
perature the amount of disorder (entropy) may be reduced by squeezing
the atoms into a smaller volume (raising the pressure) because surely
then the random motion is more confined.   In Fig. 1.4 we may go from
point α to point β by use of a compressor and remove any heat generated
by use of a heat interchanger.   The Claude expansion engine is simply a
device for allowing us to go from point β to point γ on the plot.   This is
done at constant entropy so that we may think of the pressure and tem-
perature variables as having suitably shifted to preserve the degree of
disorder.   Energy has been removed from the gas in two steps: during

the compression by the water cooling and during the expansion by means of the drive rod. The drive rod may be connected to a crankshaft so that energy may be absorbed.

With curves like that in Fig. 1.4 given for any gas, the constant-entropy condition for the expansion engine allows one to determine the temperature drop for any pressure change. We may determine the temperature drop from the gas laws and thermodynamic considerations. Since no heat is added to or taken out of the expander during the process, then by the first law $dU + P\,dV = 0$. Consider now an ideal gas for which $dU = C_v dT$ and $PV = RT$. The symbols have their usual meaning, with U the internal energy per mole of the system and C_v the specific heat at constant volume per mole of gas. We define C_p as the specific heat at constant pressure per mole of gas and γ the ratio C_p/C_v. We may differentiate the last equation above and substitute the relation $R = C_p - C_v$ and obtain $R\,dT = P\,dV + V\,dP$. Substitution gives

$$\frac{C_p P\,dV + C_v V\,dP}{C_p - C_v} + P\,dV = 0 \tag{1.8}$$

Using the ratio γ, we then have $\gamma\,dV/V + dP/P = 0$, and this equation integrates to the equation of curve bc of Fig. 1.3; $PV^{\gamma} = $ constant. We may also write this last equation in the form $TP^{(1-\gamma)/\gamma} = $ constant. Suppose we consider that the gas enters the Claude expander at a temperature T_1 and pressure P_1, and we wish to know the temperature T after the expansion to the pressure P. We may then write $TP^{(1-\gamma)/\gamma} = T_1 P_1^{(1-\gamma)/\gamma}$ and have then

$$T_1 - T = T_1\left[1 - \left(\frac{P_1}{P}\right)^{(1-\gamma)/\gamma}\right] \tag{1.9}$$

Putting in some values for helium gas, $\gamma = 1.67$, $P_1 = 15$ atm, $P = 1.1$ atm, and allowing the gas to enter the expander at $T_1 = 100°K$, we obtain $T = 40°K$. Allowing for a loss factor of 40 per cent, we still get an appreciable temperature drop. We may define the amount of refrigeration made available as $nC_p(T_1 - T)$, where n moles of gas per unit of time pass through the expander. The expanded gas passes counterflow to the incoming gas through the heat exchanger and then back to the compressor. Gradually the incoming high-pressure gas enters the expander at a lower and lower temperature. If this process continues and if the heat leaks from external sources are not too great, a liquid mist could form during the expansion stroke. The compressor would then have a maximum task of pushing a sufficient mass of gas to keep up the pressure. This limitation results in the use of the Claude expander down to such temperatures as efficiency permits, and then the last bit of cooling for liquefaction is done with the Joule-Thomson expansion valve.