VIII. Physical and chemical kinetics in hydrodynamic processes

1. Dynamics of a nonequilibrium gas

§1. The gasdynamic equations in the absence of thermodynamic equilibrium

In the preceding chapter we have studied the structure of a shock front in a gas with slow excitation of some of the degrees of freedom and have become acquainted with one of the simplest problems of nonequilibrium gasdynamics. The variables behind the shock wave front, in the region where complete thermodynamic equilibrium is established, are independent of the mechanism and the rates of the nonequilibrium processes. The rates of these processes, however, have an appreciable effect on the distribution of the hydrodynamic variables in the nonequilibrium region and on the thickness of this region. Distortions of gasdynamic flows caused by the nonequilibrium processes are attributable mainly to changes in the specific heats and in the effective specific heat ratio of the nonequilibrium gas on which the progress of the gasdynamic process depends. The effect of the specific heat ratio on gasdynamic solutions may be seen from the examples of those problems which were treated in Chapter I. Thus, in the unsteady expansion of a gas initially at rest from a tube into vacuum, the exhaust velocity is equal to \( u = 2c_0/(\gamma - 1) \) where \( c_0 = (\gamma \rho_0/\rho_0)^{1/2} \) is the speed of sound in the initial state. Let us assume that a diatomic gas, contained by a diaphragm in a tube, is initially at equilibrium and is then heated to a temperature at which the vibrational modes are "classically" excited. After the diaphragm is broken it is assumed that the gas expands so rapidly that the vibrational modes remain frozen, and that in the expansion the vibrational energy does not have sufficient time to be converted into the kinetic energy of the expansion*. This would mean that the exhaust velocity does not correspond to the equilibrium value of the specific heat ratio \( \gamma = 9/7 \) but to \( \gamma' = 7/5 \), and thus is smaller roughly by a factor of 7/5 = 1.4.

* During the expansion the density decreases, the rates of various processes are decreased, and the conversion of vibrational energy into the translational energy of the molecules, which is necessary for the subsequent conversion into the energy of directed, hydrodynamic motion, takes a long time.
This simple example shows the appreciable effect that nonequilibrium in a gas can exert on the dynamics of the process. The need to consider the rate of establishment of equilibrium arises whenever we are dealing with rapidly changing processes, or with processes whose characteristic scales are comparable with the relaxation "lengths". One of the more important practical problems of this type deals with the problem of a very rarefied gas flowing past a body, in which the relaxation times are comparable with the flow time about the body, in which the relaxation "length" is comparable with the characteristic dimensions of the body. The reentry of ballistic missiles into the atmosphere at hypersonic speeds is accompanied by the formation of a detached shock wave ahead of the body, as shown in Fig. 8.1. The distance between the shock and the nose of the body is usually of the order of one-tenth the radius of curvature of the nose. If the gas is sufficiently rarefied that there are not a sufficiently large number of gaskinetic mean free paths over the stand-off distance between the shock and the body, then the slowly relaxing degrees of freedom in the gas particles behind the shock front do not have time to become excited, or in other words, not enough time is available to establish chemical equilibrium. As a result, the temperature of the gas compressed by a shock wave is found to be higher than under conditions of thermodynamic equilibrium, and this changes the manner in which the body is heated. In fact, we are dealing here with a case in which the character of the distribution of the flow variables in the nonequilibrium region which forms behind the compression shock is rather important.

In a number of cases it is possible to approximately describe the dynamics of a nonequilibrium gas by using some effective value of the specific heat ratio, corresponding to some degree of freezing of part of the specific heat, as for example when the energy change in some degrees of freedom can be neglected over the characteristic hydrodynamic flow time. In general, however, one must consider the gasdynamic process simultaneously with the kinetics of the nonequilibrium processes, which complicates the system of equations describing the phenomenon.

The dynamics of a nonviscous and nonheat-conducting gas at thermodynamic equilibrium is described by the equations of continuity, momentum,
and entropy:

\[ \frac{D\rho}{Dt} + \rho \nabla \cdot \mathbf{u} = 0, \quad (8.1) \]
\[ \rho \frac{Du}{Dt} + \nabla p = 0, \quad (8.2) \]
\[ \frac{DS}{Dt} = 0, \quad (8.3) \]

to which we add the thermodynamic relationship for entropy as a function of pressure and density, \( S(p, \rho) \) (for example, in a gas with constant specific heats \( S = c_v \ln(p\rho^{-\gamma}) + \text{const} \)).

We shall now consider the motion of a gas whose state departs from thermodynamic equilibrium. Here again we shall neglect viscosity and heat conduction and assume that the nonequilibrium state is entirely connected with the delayed progress of internal processes which take place only within a given parcel of the fluid, such as, for example, the delayed excitation of molecular vibrations.

In the case of nonequilibrium we replace the entropy equation (8.3), which no longer applies, by the more general equation of conservation of energy, which is always valid. Assuming the absence of any external energy sources*, we can write in place of (8.3)

\[ \frac{D\varepsilon}{Dt} + p \frac{DV}{Dt} = 0. \quad (8.4) \]

By virtue of the thermodynamic identity

\[ T \, dS = d\varepsilon + p \, dV \quad (8.5) \]

(8.4) and (8.3) are equivalent under conditions of thermodynamic equilibrium. While in the equilibrium case the internal energy \( \varepsilon \) is determined by the pressure and density only, \( \varepsilon = \varepsilon(p, \rho) \), in the absence of equilibrium it also depends on other variables characterizing the state of the system which are not in equilibrium (for example, on the degree of dissociation). Without specifying these parameters, we shall term them \( \lambda \). To close the system of gasdynamic equations, we must add to (8.1), (8.2), and (8.4) an equation

* The thermal effect of a reversible chemical reaction is not an external energy source; it is taken into account by introducing an appropriate term into the expression for the internal energy of the gas.
connecting the internal energy with the pressure, density, and the state variables \( \lambda \),

\[ \varepsilon = \varepsilon(p, \rho, \lambda), \]

and also rate equations which describe the changes in the variables \( \lambda \) in the gas with time,

\[ \frac{D\lambda}{Dt} = f(\lambda, p, \rho). \]

Usually, the functions \( \varepsilon(p, \rho, \lambda) \) and \( f(\lambda, p, \rho) \) are not expressed explicitly in terms of density and pressure, but instead in terms of temperature

\[ \varepsilon = \varepsilon(\rho, T, \lambda), \quad \frac{D\lambda}{Dt} = f(\lambda, \rho, T). \]

In this case, we must also add the equation of state

\[ p = p(T, \rho, \lambda). \]

The temperature \( T \), unless otherwise noted, will always denote the temperature corresponding to the translational degrees of freedom of the molecules (atoms, ions). These are usually in equilibrium even in the most rapid gasdynamic processes, since the Maxwell distribution of molecular velocities is established extremely rapidly.

As an example of a nonequilibrium system let us consider a diatomic gas without dissociation but with slow excitation of the vibrational modes of the molecule (we consider only not too high temperatures, for which the degree of dissociation is still negligibly small). The role of the variable \( \lambda \) is played here by the nonequilibrium vibrational energy \( \varepsilon_{\text{vib}} \) (per unit mass of the gas). For the given case, the equations which must be added to the system, (8.1), (8.2), and (8.4), may be written in the form

\[ \varepsilon = \varepsilon_t + \varepsilon_{\text{vib}} = \frac{1}{2}RT + \varepsilon_{\text{vib}}, \quad (8.6) \]

\[ p = R\rho T, \quad (8.7) \]

\[ \frac{D\varepsilon_{\text{vib}}}{Dt} = \frac{\varepsilon_{\text{vib}}(T) - \varepsilon_{\text{vib}}}{\tau(T, \rho)}. \quad (8.8) \]

Here \( \varepsilon_t \) is the sum of the energies of the translational and rotational degrees of freedom of the molecules. (It is assumed that the rotational energy has its equilibrium value, and corresponds to the translational temperature \( T \).) The quantity \( \varepsilon_{\text{vib}}(T) \) is the vibrational energy which the gas would have in thermodynamic equilibrium with the translational degrees of freedom, and \( \tau(T, \rho) \) is the relaxation time for establishing vibrational equilibrium.
Similar equations which are, however, of a more complex form, can also be written for all the other cases, where there is nonequilibrium dissociation, chemical reactions, ionization, or where the translational temperatures of the electron and atom (ion) gases differ. All these cases were examined in the preceding chapter when we considered the structure of the nonequilibrium layer in a shock front.

§2. Entropy increase

An extremely important property of nonequilibrium gasdynamic processes is the increase in the entropy of the gas and the dissipation of mechanical energy. As with the internal energy \( \varepsilon \), the entropy of a nonequilibrium gas is no longer determined by only the two variables pressure and density or temperature and density, but depends on the other variables which characterize the nonequilibrium state; thus \( S = S(p, \rho, \lambda) \) or \( S(T, \rho, \lambda) \). The increase in entropy \( dS \) is no longer equal to the heat supplied by the external sources divided by temperature, as was true for the equilibrium case, so \( dS \neq dQ/T \). The entropy increases with time even without a supply of heat (when \( dQ = 0 \)) as a result of the nonequilibrium internal processes only.

We shall clarify our preceding remarks with the aid of the example of nonequilibrium vibrational excitation. The total specific entropy of a gas \( S \) is composed of the entropies corresponding to the translational and rotational degrees of freedom, which because of their equilibrium character can be combined, plus the vibrational entropy*. We denote these two parts of the entropy by \( S_1 \) and \( S_{\text{vib}} \), respectively, with

\[
S = S_1 + S_{\text{vib}}. \tag{8.9}
\]

For the entropy of the translational and rotational degrees of freedom we can write the thermodynamic relation

\[
T \, dS_1 = d\varepsilon_1 + p \, dV. \tag{8.10}
\]

Usually, the exchange of vibrational energy by molecules takes place much faster than the exchange between the vibrational and translational energies. Thus a Boltzmann distribution with respect to the vibrational excitations of the molecules is established quite rapidly, and we can assign a definite temperature \( T_{\text{vib}} \) to the vibrations. This temperature corresponds to the actual supply of vibrational energy \( \varepsilon_{\text{vib}} = \varepsilon_{\text{vib}}(T_{\text{vib}}) \). If we denote the vibrational specific heat by \( c_{\text{vib}} \), then \( d\varepsilon_{\text{vib}} = c_{\text{vib}} \, dT_{\text{vib}} \). Here, of course, the

* For nonequilibrium dissociation or ionization an expression for the entropy is written in terms of the number of different species of particles (molecules and atoms, for example) which are assumed to be out of equilibrium.
vibrational temperature $T_{\text{vib}}$ can be appreciably different from the translational temperature of the molecules $T$; this difference is the manifestation of the nonequilibrium state of the gas*. If we can assign the specific temperature $T_{\text{vib}}$ to the vibrational modes, then for the vibrational contribution to the entropy we can also write the thermodynamic relation

$$T_{\text{vib}} \, dS_{\text{vib}} = d\varepsilon_{\text{vib}}. \quad (8.11)$$

The vibrational energy and entropy are independent of the gas volume.

It is easy to see that the entropy of a nonequilibrium system only increases with time, independent of the transformations the gas undergoes. Indeed, by virtue of (8.9), (8.10), (8.4), and (8.6), we have

$$\frac{DS}{Dt} = \frac{DS_1}{Dt} + \frac{DS_{\text{vib}}}{Dt} = \frac{1}{T} \left( \frac{D\varepsilon_1}{Dt} + p \frac{DV}{Dt} \right) + \frac{1}{T_{\text{vib}}} \frac{D\varepsilon_{\text{vib}}}{Dt} = \frac{D\varepsilon_{\text{vib}}}{Dt} \left( \frac{1}{T_{\text{vib}}} - \frac{1}{T} \right). \quad (8.12)$$

Taking into account the rate equation (8.8) in which

$$\varepsilon_{\text{vib}} = \int_0^{T_{\text{vib}}} c_{\text{vib}}(T') \, dT' \quad \text{and} \quad \varepsilon_{\text{vib}}(T) = \int_0^T c_{\text{vib}}(T') \, dT',$n

we see that for $T_{\text{vib}} < T$ the vibrational modes take away energy from the translational and rotational degrees of freedom, $D\varepsilon_{\text{vib}}/Dt > 0$, and $DS/Dt > 0$. For $T_{\text{vib}} > T$ the vibrations give up their energy $D\varepsilon_{\text{vib}}/Dt < 0$, but again $DS/Dt > 0$. The above example illustrates the second law of thermodynamics according to which, without the participation of external factors, heat is always transferred from the hotter to the cooler object, and as a result of which the entropy of the entire system increases. In our case the "objects" are not bodies touching one another, but different degrees of freedom of the same body.

If at a given time the gas is in a state of thermodynamic equilibrium, and it then takes part in a rapidly progressing process during which the equilibrium is disturbed and subsequently the state of the gas changes slowly in order to return to equilibrium, then the entropy of the gas will increase. This increase in entropy is accompanied by the dissipation of mechanical energy, namely by its irreversible conversion into heat. If the process proceeds without the participation of external energy sources, satisfying the energy equation (8.4), then the dissipated energy cannot under any conditions be again converted into mechanical energy. We shall study the phenomenon

* We recall that a similar situation occurs in the case of a plasma. The Maxwell distributions and the temperatures in the electron and ion gases are established very rapidly. The electron and ion temperatures, however, differ from each other as a result of the slow exchange of energy between the electron and ion gases.
§3. Anomalous dispersion and absorption of ultrasound

Anomalous dispersion and absorption of ultrasound are phenomena that occur in gases at very short wavelengths, typically those comparable to the mean free path of the gas particles. These phenomena are characterized by the dissipation of mechanical energy in the form of sound waves. Absorption and dispersion are connected with processes such as viscosity and heat conduction, but become significant only at frequencies comparable to the gaskinetic collision frequency, as discussed in §22 of Chapter I.

Dispersion and absorption of sound in gases are phenomena that have significant implications for the study of gasdynamic processes. These processes play a crucial role in the propagation of sound waves through relaxing mediums, and their understanding is essential for the accurate prediction of wave behavior in complex environments. As such, the study of these phenomena is a fundamental aspect of gas dynamics.
waves in molecular gases is, however, sometimes accompanied by an anomalously strong dispersion and absorption in a region of much greater wavelengths and lower frequencies. These phenomena are related to the relaxation processes for the establishment of equilibrium in slowly excited degrees of freedom of the gas.

In the limiting case of low frequencies, the relaxation times for establishing equilibrium in those degrees of freedom which make an appreciable contribution to the specific heat are small in comparison with the period of sound vibrations. Under these conditions a gas particle is in a state of thermodynamic equilibrium at any instant of time, and "follows" the changes in pressure and density in the sound wave. The speed of sound, defined as the square root of the isentropic derivative of the pressure with respect to density, corresponds to its own thermodynamic equilibrium value

$$a^2 = \left( \frac{\partial p}{\partial \rho} \right)_S = \gamma \frac{p_0}{\rho_0}, \quad \gamma = \frac{c_p}{c_v} = 1 + \frac{R}{c_v}. \quad (8.13)$$

On the other hand, in the limiting case of very high frequencies, the slowly relaxing degrees of freedom in the sound wave do not have time to become excited, and their energy simply corresponds to the temperature of the undisturbed state $T_0$. These degrees of freedom do not participate in the periodic changes in the state of the gas; they are "frozen", and do not affect the isentropic relationship between the changes in pressure and density. The active part of the specific heat is now less than at equilibrium, and the specific heat ratio and the speed of sound are greater than at low frequencies.

A gradual change of the speed of sound from the equilibrium value $a_0$ to the value $a_\infty$ corresponding to the frozen part of the specific heat takes place in the intermediate frequency region; thus, there is dispersion of sound. For example, measurements of Kneser [3, 4] show the speed of sound in carbon dioxide at room temperature to vary between $a_0 = 260$ m/sec at a frequency $\nu$ of the order of $10^4$ sec$^{-1}$ (10 kc) to $a_\infty = 270$ m/sec at $\nu \sim 10^6$ sec$^{-1}$ (1 Mc). The lower speed of sound corresponds to the equilibrium value of the specific heat

$$c_v = c_{trans} + c_{rot} + c_{vib} = \frac{3}{2}R + R + 0.8R = 3.3R.$$  

The CO$_2$ molecule is linear, so that $c_{rot} = R$; only the low-frequency molecular vibrations with $\hbar\nu/k = 954^\circ$K are excited at room temperature, and for these the vibrational specific heat is even smaller than its classical value $R$. The higher speed of sound corresponds to frozen vibrations, with a specific heat $c_v = c_{trans} + c_{rot} = 2.5R$. It follows from these data that the relaxation time for vibrational excitation in a CO$_2$ molecule (at atmospheric pressure)

* We are here using specific heat capacities; $R$ is the gas constant per unit mass. To avoid confusion, we denote the speed of sound here by $a$ instead of $c$.  

(8.13)
corresponds to some intermediate sound frequency, so that roughly \( \tau_{\text{vib}} \sim 1/\nu \sim 10^{-5} \) sec. Molecular rotations at room temperature are excited very rapidly and dispersion related to slow rotational excitation can be observed at atmospheric pressure only at extremely high frequencies \( \nu \sim 1/\tau_{\text{rot}} \sim 10^9-10^{10} \text{sec}^{-1} \) (the only exception is hydrogen; see §2, Chapter VI).

Dispersion of sound is also observed in gases in which slow chemical reactions take place as a result of the temperature (and density) changes in a sound wave. An example is the polymerization of nitrogen dioxide \( 2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4 \), which takes place easily at room temperature since its heat of activation in both directions is very low. It was in connection with systems of this type that the theory of sound dispersion was first developed by Einstein in 1920 [5]. Apparently, analogous phenomena also occur in the propagation of ultrasound in some liquids.

Measurements of ultrasonic dispersion and absorption provide one of the most important methods of studying relaxational processes and of experimentally determining relaxation times. There is an extensive literature devoted to this subject* but we shall not consider it in detail here. We shall examine only the basic physical properties and laws governing this phenomenon.

Dispersion of sound in a relaxing fluid is always accompanied by increased absorption, which considerably exceeds the natural absorption due to ordinary viscosity and heat conduction. A fluid parcel in a sound wave performs successive cyclical transformations, returning to its initial state upon the completion of each cycle. If internal nonequilibrium processes take place in the parcel, they inevitably lead to an increase in entropy and to a dissipation of mechanical energy, and thereby to the absorption of sound. It is to be emphasized that in the presence of dissipation the state of a parcel upon completion of a cycle differs somewhat from its initial state (since its entropy increases). However, this difference, let us say the temperature increase, is proportional to the entropy increase, and is a second-order quantity in comparison with the small amplitude of the sound wave \( \Delta \rho \) or \( \Delta T \). This follows from the fact that the entropy increase \( \Delta S \) is proportional to the sound energy which, in turn, is proportional to \( (\Delta \rho)^2 \) (see §3, Chapter I). Therefore, in first approximation the motion in a sound wave even in the presence of absorption is isentropic and we can regard the cycles to be closed.

The mechanism of dissipation of mechanical energy and of sound absorption can be made clearer by considering the cycle in the gas on a \( p, V \) diagram. Figure 8.2 shows two families of isentropes, one of which (I) corresponds to equilibrium changes of state, and the other (II) to the frozen part of the specific heat. The isentropes were drawn near the undisturbed region, denoted

* A survey of the literature and references may be found, for example, in [6].
by the point $O$. For very slow sound vibrations the point describing the state of the gas, $p$, $V$, oscillates about the center $O$ along the equilibrium isentrope, denoted in Fig. 8.2 by $I'$. In the limiting case of very high frequency, the point oscillates about the center along the "frozen" isentrope denoted by $II'$. In both cases nonequilibrium processes are absent, the entropy of the gas does not change, and there is no sound absorption. The work done on the gas per cycle, which is numerically equal to the area of the figure described by the point on the $p$, $V$ diagram, is equal to zero, which shows that absorption is absent. Using the example of vibrational relaxation it is easy to see that the entropy of the gas does not change in the second case, as well as in the first case of thermodynamic equilibrium. It is evident from (8.12) that the rate of change of the entropy in a nonequilibrium process is proportional to the rate of change of the vibrational energy. But, for strictly frozen vibrational modes this energy does not change, $e_{vib} = const$, and $DS/DT = 0$.

Let us now consider sound waves of intermediate frequencies, where relaxation processes are important (for definiteness we again consider vibrational relaxation). For simplicity we imagine that the density profile in the sound wave has the square wave shape shown in Fig. 8.3a*. This plot can be considered either as a density distribution with respect to the position coordinate at a given instant of time, or as the relation governing the change in density in a given gas particle with time. The same applied to Fig. 8.3b, which illustrates the corresponding temperature (or pressure) profiles (the temperature and pressure profiles are in this case similar).

We shall follow the change of state of a gas particle in a wave on the $p$, $V$ diagram of Fig. 8.2, as well as on Figs. 8.3a and b. When the gas is very rapidly compressed from point $A$ to point $B$, its state changes along a frozen isentrope $II$. In this case the entropy does not change, and positive work, numerically equal to the area $NABM$, is done on the gas. The gas temperature and pressure increase sharply while the vibrational energy remains unchanged.

* This example, which is distinguished by its clarity, has been considered before, for example in the book by Gorelik [7].
and corresponds to the old, low temperature. Then, for a certain period of time, the gas density remains unchanged (the transition $B \rightarrow C$). The vibrational modes are excited, part of the energy is transferred from the transla-

tional and rotational degrees of freedom, the temperature and pressure decrease, and the entropy increases (see (8.12): $T_{\text{vib}} < T$, $-De_{\text{vib}}/Dt > 0$, and $DS/DT > 0$). Since the volume does not change, no work is performed during the transition $B \rightarrow C$.

Following this the gas then expands very rapidly (the transition $C \rightarrow D$) along a frozen isentrope II. The temperature and pressure fall, the entropy remains unchanged, and the vibrational energy also remains unchanged at the value it had at point $C$. The work done by the gas is numerically equal to the area $MC\!D\!N$ (negative work is done on the gas). And, finally, during the slow transition at constant volume $D \rightarrow A$, the vibrational modes are partially deexcited since their energy exceeds the value corresponding to the decreased temperature; the vibrational energy is partially transformed into translational and rotational energy, the temperature and pressure increase, and the entropy also increases ($T_{\text{vib}} > T$, $-De_{\text{vib}}/Dt < 0$, $DS/DT > 0$). No work is done in this case.

Thus, during the expansion stage $C \rightarrow D$ the gas particle does less work on the surrounding gas than done by the gas on the particle during the compression stage $A \rightarrow B$. The particle does not fully “give back” the work. Part of the energy expended during the compression period remains “forever” in the particle. This energy, numerically equal to the difference in work, to the area of the figure $ABCD$, is the mechanical energy which has been irreversibly converted into heat. As a result of the dissipation of mechanical energy the sound wave is also attenuated (absorbed); the absorption of
sound energy per period (or per wavelength) is exactly equal to the area $ABCD$.

On the other hand, irreversible generation of heat is related to the entropy increase per cycle, and is equal to $T_0 \Delta S$. This quantity, as is evident from Fig. 8.2, is proportional to $\Delta V \cdot \Delta p \sim (\Delta p)^2$. It follows therefore that the displacement of the final state point $A'$ relative to the initial state point $A$, $\delta p = (\partial p/\partial S)_V \cdot \Delta S \sim (\Delta p)^2$, is a second-order quantity with respect to the amplitude $\Delta p$. Since $(\partial p/\partial S)_V > 0$, $\delta p > 0$, that is, the pressure upon completion of the cycle is slightly higher than the initial pressure. Similarly, the temperature is also slightly higher, $\delta T = (\partial T/\partial S)_V \Delta S = T_0 \Delta S/c_v \approx T_0 \Delta S/c_v$. The temperature increase is equal to the energy dissipated per cycle, divided by the specific heat at constant volume.

In a sinusoidal (harmonic) sound wave a point on the $p, V$ diagram describes a smooth curve. All the state variables, density, pressure, and temperature vary harmonically with time. However, due to the slow excitation and deexcitation of molecular vibrations, the temperature or pressure changes cannot follow the density changes and the sinusoidal pressure variation undergoes a phase shift with respect to the sinusoidal variation in density (volume). It can be shown that a point on the $p, V$ diagram describes, in this case, an elliptical trajectory, with the axes of the ellipse inclined with respect to the $p, V$ coordinate axes.

At low frequencies $\nu$ (or angular frequencies $\omega = 2\pi \nu$) the ellipse is stretched out along an equilibrium isentrope (see curve 1 in Fig. 8.4). The thickness of

![Fig. 8.4. $p, V$ diagram for the cycles in harmonic sound waves of different frequencies.](image)

the ellipse in the limit of small frequencies is proportional to the frequency (to the first term of an expansion in the small quantity $\omega$). The sound energy absorbed per period is proportional to $\omega$ and that absorbed per unit time is proportional to the number of cycles, that is, to $\omega^2$. At high frequencies the ellipse is stretched out along a frozen isentrope (curve 2). The thickness of the ellipse is proportional to $1/\omega$ (as can also be seen from an expansion), and the absorption per unit time is proportional to $\omega \cdot 1/\omega$, that is, it is
§4. Dispersion law and absorption coefficient for ultrasound

The qualitative considerations on the dispersion and absorption of sound in the presence of relaxation processes in a fluid presented in the preceding section can be put into an elegant mathematical form. This was done in a general form by Mandel'shtam and Leontovich* [8]; dispersion and absorption relations, in which the relaxation time $\tau$ appears, usually serve to determine that time from the experimentally measured dispersion or absorption curves as a function of the ultrasonic frequency.

Let us show how we may derive the dispersion relation and the expression for the absorption coefficient in a relaxing medium. For simplicity and clarity we shall carry out the calculation using the specific example of a gas with nonequilibrium vibrational modes, for which the complete system of gasdynamic equations (8.1), (8.2), (8.4), (8.6), (8.7), and (8.8) has been formulated in §1. All the variables in the sound wave, pressure, density, etc., will be written in the form $f = f_0 + f'$, where $f_0$ is the average value corresponding to the undisturbed gas and $f'$ is a variable part or perturbation, which will be considered a small quantity (the velocity $u = u_0 + u' = u'$, since the undisturbed gas is at rest and $u_0 = 0$). The true vibrational energy can also be expressed as $\varepsilon_{\text{vib}} = \varepsilon_{\text{vib0}} + \varepsilon_{\text{vib}}'$, where $\varepsilon_{\text{vib0}}$ is the vibrational energy in the undisturbed gas at equilibrium. The perturbation of the equilibrium vibrational energy we shall write in the form $\varepsilon_{\text{vib}}'(T) = c_{\text{vib}}T'$, where $c_{\text{vib}}$ is the vibrational specific heat corresponding to the average temperature $T_0$ (if at $T_0$ the vibrational modes have their classical value, then $c_{\text{vib}} = R$, while if this is not the case, $c_{\text{vib}}$ is expressed by a quantum-mechanical relation; see §2, Chapter III).

* A presentation of this theory may be found in the book by Landau and Lifshitz [9].
Let us substitute into the equations all of the quantities in the form indicated above and neglect second-order terms, thus linearizing the equations as is usual in acoustics (see §3 of Chapter I). We then obtain for the one-dimensional plane case the following system of equations for the perturbations

$$\begin{align*}
\frac{\partial p'}{\partial t} + \rho_0 \frac{\partial u'}{\partial x} &= 0, \\
\frac{\partial u'}{\partial t} + \frac{1}{\rho_0} \frac{\partial p'}{\partial x} &= 0, \\
\frac{\partial \varepsilon'}{\partial t} - \frac{p_0}{\rho_0^2} \frac{\partial p'}{\partial t} &= 0, \\
\frac{\partial \varepsilon_{\text{vib}}'}{\partial t} &= \frac{c_{\text{vib}} T'}{\tau} - \varepsilon_{\text{vib}}'.
\end{align*}$$

(8.14)

Here the specific volume in the energy equation (8.4) has been replaced by the density, and both sides of the equation of state have been divided by $p_0 = R \rho_0 T_0$. The relaxation time $\tau$ is taken to be constant and given by $\tau = \tau(T_0, \rho_0)$.

A solution of the system (8.14) will be sought in the form of a harmonic plane wave, with all the primed quantities expressed in the form

$$f' = f'^* e^{-i(\omega t - kx)}. \quad (8.15)$$

The wave number $k$ is in general complex: $k = k_1 + ik_2$. The real part $k_1$ is proportional to the reciprocal of the wavelength $k_1 = 2\pi/\lambda$ and determines the actual speed of sound—the phase velocity of wave propagation $a_1 = \omega/k_1$; the imaginary part $k_2$ gives the sound absorption coefficient

$$f' = f'^* e^{-i\omega t - kx} e^{-k_2 x}. \quad (8.16)$$

The quantity $a = \omega/k$ may be called the complex speed of sound. The amplitudes $f'^*$ are in general also complex, with $f'^* = |f'^*| e^{i\varphi}$. The complex character of the amplitudes testifies to the phase shifts of some of the quantities with respect to the others (through the differences of the angles $\varphi$).

Substituting into (8.14) all of the quantities in the form defined by (8.15) and noting that $\partial f'/\partial t = -i\omega f'$, $\partial f'/\partial x = ikf'$ we obtain a system of algebraic equations for the primed quantities (or for the amplitudes, if we cancel out the exponential factor)

$$\begin{align*}
-i\omega p' + \rho_0 k u' &= 0, \\
-i\omega u' + \frac{1}{\rho_0} k p' &= 0, \\
-i\omega \varepsilon' + \frac{p_0}{\rho_0^2} i\omega p' &= 0,
\end{align*}$$

$$\begin{align*}
\varepsilon' &= \frac{1}{2} R T' + \varepsilon_{\text{vib}}', \\
\frac{p'}{\rho_0} &= \frac{T'}{T_0} + \frac{\rho'}{\rho_0}, \\
-\omega \varepsilon_{\text{vib}}' &= \frac{c_{\text{vib}} T'}{\tau} - \varepsilon_{\text{vib}}'.
\end{align*}$$

(8.17)
§4. Dispersion law and absorption coefficient for ultrasound

Solving the last equation for \( \varepsilon'_{\text{vib}} \) we obtain

\[
\varepsilon'_{\text{vib}} = \frac{c_{\text{vib}} T'}{1 - i\omega\tau}.
\]  

(8.18)

It is precisely this complex relation between the perturbations of the true vibrational energy and of the temperature that causes dispersion and absorption to arise. It can already be seen from this relation that in the limiting cases \( \omega\tau \to 0 \) and \( \omega\tau \to \infty \), for which \( \varepsilon'_{\text{vib}} = c_{\text{vib}} T' \) and \( \varepsilon'_{\text{vib}} = 0 \), the imaginary unit \( i \) drops out completely from the system of equations (8.17) and all the quantities are real (if \( \rho' \), \( \rho'' \), etc., are understood to denote the amplitudes \( \rho'^* \), \( \rho''^* \), etc.). Neither absorptions nor phase shifts occur in this case.

The first two equations of the system (8.17), which were obtained from the equations of continuity and motion by eliminating the velocity, yield the usual relationship

\[
p' = \frac{\omega^2}{k^2} \rho' = a^2 \rho',
\]  

(8.19)

where \( a \) is now the complex speed of sound. Eliminating \( \varepsilon' \), \( \varepsilon'_{\text{vib}} \), and \( T' \) from the remaining four equations, we obtain still another relationship between \( p' \) and \( \rho' \),

\[
p' = \frac{\gamma}{\rho_0} \rho', \quad \gamma = \frac{\frac{1}{2}R + c_{\text{vib}}/(1 - i\omega\tau)}{\frac{3}{2}R + c_{\text{vib}}/(1 - i\omega\tau)}.
\]  

(8.20)

The quantity \( \gamma \) may be termed the complex specific heat ratio. Introducing the notation where \( c_{\text{vib}} = \frac{1}{2}R + c_{\text{vib}} \) and \( c_{p_0} = \frac{3}{2}R + c_{\text{vib}} \) are the equilibrium specific heats at constant volume and pressure, respectively, and \( c_{v_0} = \frac{1}{2}R \) and \( c_{p_\infty} = \frac{3}{2}R \) are the specific heats with the vibrational modes completely frozen, we can write the complex specific heat ratio and the expression for the complex speed of sound, from (8.19) and (8.20), as

\[
a^2 = \frac{\gamma}{\rho_0} \rho_0, \quad \gamma = \frac{c_{p_0} - i\omega\tau c_{p_\infty}}{c_{v_0} - i\omega\tau c_{v_\infty}}.
\]  

(8.21)

* Landau and Lifshitz derive a slightly different equation in their book [9] (Chapter VIII, §78, equations (78.3)),

\[
\gamma = \frac{1}{1 - i\omega\tau} \left[ c_{p_0} - i\omega\tau c_{p_\infty} \right].
\]

This difference arises from a difference in the definitions of the relaxation time \( \tau \) which enters in the rate equation. The quantity \( \varepsilon_{\text{vib}}(T) \) in our equation (8.8) represents the equilibrium vibrational energy which corresponds to the translational temperature \( T \). Let us denote the relaxation time in our rate equation by the subscript " \( \tau \) " and the translational temperature is also maintained constant: \( T = \text{const} \), then
In the limiting case of very low frequencies $\omega \tau \ll 1$, $\gamma = c_{p\infty}/c_{v\infty} = \gamma_\infty$, $a^2 = \gamma_\infty p_\infty / \rho_0 = a_\infty^2$, we obtain the equilibrium specific heat ratio and speed of sound. In the limit of high frequencies $\omega \tau \gg 1$,

$$\gamma = \frac{c_{p\infty}}{c_{v\infty}} = \gamma_\infty,$$

$$a^2 = \gamma_\infty \frac{p_\infty}{\rho_0} = a_\infty^2,$$

we obtain a specific heat ratio and a speed of sound corresponding to frozen vibrational modes. In both limiting cases the speed of sound and consequently the wave number, $k = \omega/a$, are real, and there is no absorption.

(8.8) gives an exponential relationship with a characteristic time $\tau_\gamma$ for the approach to equilibrium

$$\varepsilon_{vib} = \varepsilon_{vib}(T) + \left[ (\varepsilon_{vib})_{T=0} - \varepsilon_{vib}(T) \right] e^{-\frac{\varepsilon_{vib}(T)}{k_B T}}$$

The energy of the gas $\varepsilon = c_{v\infty} T + \varepsilon_{vib}$ is not constant in this case. However, if we assume that the total energy (and, of course, the volume) is constant and use (8.8), then instead of a simple exponential law we obtain a more complex law governing the approach to equilibrium.

Landau and Lifshitz [9] write a rate equation of the type (8.8), but defined so that the equilibrium energy term denotes the vibrational energy at an equilibrium temperature $T_{eq}$ which corresponds to both the translational and vibrational degrees of freedom, and which thus depends on the given volume $V$ and total energy $\varepsilon$ of the gas. Let us denote the relaxation time which enters in this rate equation (according to [9]) by $\tau_S$. The equation yields the exponential relationship for the approach to equilibrium

$$\varepsilon_{vib} = \varepsilon_{vib}(T_{eq}) + \left[ (\varepsilon_{vib})_{T=0} - \varepsilon_{vib}(T_{eq}) \right] e^{-\frac{\varepsilon_{vib}(T_{eq})}{k_B T_S}}$$

if the gas volume, the energy (i.e., the equilibrium temperature $T_{eq}$), and the time $\tau_S$ are constant. Actually, $\tau_S$ depends on the translational temperature, but it is assumed that the departure from equilibrium is slight, so that at $T_{eq} = const$ the translational temperature changes only very little. For a slight departure from equilibrium, we can consider the condition $V = const$, $\varepsilon = const$ as a condition of approximate constancy of the entropy, $S \approx const$.

Let us consider small changes of all quantities in a sound wave about their average values. Using the definition

$$\varepsilon' = c_{v\infty} T' + \varepsilon_{vib} = c_{v\infty} T_{eq} + \varepsilon_{vib}(T_{eq}) = c_{v\infty} T_{eq},$$

we can transform one rate equation to the other. In so doing, we find that $\tau_S = (c_{v\infty}/c_{v\infty}) \tau_\gamma$. In the equation for $\gamma$ given at the beginning of this footnote, $\tau$ should be understood to denote $\tau_S$, and in our equation (8.21) it should denote $\tau_\gamma$. By using the relationship between $\tau_S$ and $\tau_\gamma$ we can easily verify that these equations are identical.

The "$\tau_\gamma$" method, used by Mandel'shtam and Leontovich [8], makes it possible to obtain the general equation for $\gamma$ given above, independently of the actual relaxation mechanism. When considering the particular case of vibrational relaxation it is more convenient to use the "$\tau_\gamma$" method, as was done in this text. Let us note that this is the same manner in which vibrational relaxation in ultrasound was considered in older works (Kneser [3], Landau and Teller [10]).
In the intermediate frequency region, the sound speed $a$ and the wave number $k = \omega/a$ are complex. If we set up an equation for $k = \omega/a$ using (8.21) and separate the real and imaginary parts, we obtain the dispersion relation $a_1(\omega) = \omega/k_1(\omega)$ and the absorption coefficient $k_2(\omega)$. In general, this leads to rather cumbersome expressions. In the limit of low frequencies $\omega \tau \ll 1$, we obtain approximately

$$k = k_1 + ik_2 = \frac{\omega}{a_0} + i \frac{\omega^2 \tau}{2a_0 c_{p_0}} \left( \frac{\gamma_\infty}{\gamma_0} - 1 \right).$$

(8.22)

The absorption coefficient is of the order $k_2 \sim \omega^2$; the absorption over a distance of one wavelength is of the order $k_2 \lambda \sim \omega$. In the limit of high frequencies $\omega \tau \gg 1$, we have

$$k = k_1 + ik_2 = \frac{\omega}{a_\infty} + i \frac{1}{2a_\infty c_{p_\infty}} \left( \frac{\gamma_\infty}{\gamma_0} - 1 \right).$$

(8.23)

The absorption coefficient $k_2 \approx \text{const}$ is independent of the frequency, and the absorption over a wavelength is of the order $k_2 \lambda \sim 1/\omega$. The dispersion curve $a_1(\omega)$ and the frequency dependence of the absorption over a wavelength $k_2 \lambda = k_2 a_1 2\pi/\omega = 2\pi k_2/k_1$ are shown schematically in Fig. 8.5. It is not difficult to show that the quantity $k_2/k_1$ has a maximum at $\omega \tau = (c_0 c_{p_0}/c_{v_0} c_{p_\infty})^{1/2} \sim 1$. For a value of $\omega \tau$ which is close to but different from the above value, the dispersion curve has an inflection point.

It follows from (8.19) that the pressure in the sound wave is shifted in phase relative to the density. In fact, if the speed of sound is a complex quantity, then $p' = a^2 \rho' = |a^2|e^{i\phi}p'$. In the limiting cases $\omega \tau \ll 1$ and $\omega \tau \gg 1$, where the imaginary part of the speed of sound tends to zero, the

* Let us note that between the functions $k_1(\omega)$ and $k_2(\omega)$ there exists a perfectly general relationship, independent of the dispersion and absorption mechanism. This relationship was first derived by Ginzburg [11].
phase shift $\varphi$ vanishes. For $\omega \tau \sim 1$, for which the real and imaginary parts are comparable, the phase shift $\varphi$ is appreciable.

If several nonequilibrium processes with appreciably different relaxation times take place in the fluid, strong absorption and dispersion occurs whenever $\omega \tau \sim 1$ and these frequency regions are clearly separated. However, in the case of relaxation times that are only slightly different from each other the regions merge, and it is difficult to separate them experimentally to obtain the relaxation times from experimental data.

Dispersion and absorption of sound related to nonequilibrium processes are determined by fluctuations in the fluid density, and by virtue of the continuity equation $D\rho/Dt + \rho \nabla \cdot \mathbf{u} = 0$ are related to the divergence of the velocity. They can be formally described by the second coefficient of viscosity $\mu'$, which characterizes the dissipation term in the equation of motion which is proportional to the divergence of the velocity (see §§20 and 21 of Chapter I). The second coefficient of viscosity can be formally related to the quantity $\tau$ and to the limiting speeds of sound $a_0$ and $a_\infty$ (see, for example, [9]). The use of the second coefficient of viscosity in describing anomalous absorption is only possible at not too high frequencies ($\omega \tau \ll 1$). Due to viscosity the absorption coefficient increases in proportion to $k^2 \sim \omega^2$ (see §22, Chapter I). Therefore, as $\omega \to \infty$ viscous absorption increases without limit, while actually the coefficient of anomalous absorption as $\omega \to \infty$ tends to a constant value $k^2 = \text{const}$ (see equation (8.23)).

Some experimental data on the relaxation times for the excitation of molecular vibrational and rotational modes obtained by means of ultrasonic dispersion and absorption have already been presented in §§2 and 4 of Chapter VI.

2. **Chemical reactions**

§5. **Oxidation of nitrogen in strong explosions in air**

Atmospheric air consists of nitrogen and oxygen molecules; chemically it is in equilibrium and very stable. Dissociation of the molecules into atoms or their partial transformation into molecules of nitric oxide NO requires heating of the air to temperatures of several thousand degrees. The reaction of nitrogen oxidation requires a large activation energy. The activation energy required for breaking up the oxide molecules into oxygen and nitrogen is somewhat lower, but it is still large. Therefore, despite the ease from the point of view of energy considerations of transforming nitric oxide into oxygen and nitrogen at low temperatures, NO molecules are extremely stable.
It was shown in §8 of Chapter VI that if the time required for establishing the equilibrium concentration of nitric oxide in air of standard density at 4000°K is \( \sim 10^{-6} \) sec, then at 2000°K it is approximately equal to 1 sec, and at 1000°K it has the colossal value of the order of \( 10^{12} \) sec, approximately 30 thousand years! Once the nitric oxide has been formed and cooled to normal temperature it remains in air for an indefinitely long time. Actually, the oxidized nitrogen remains in the form of the dioxide \( \text{NO}_2 \) (or of \( \text{N}_2\text{O}_4 \) complexes, the preferred form for \( \text{NO}_2 \) molecules), since nitric oxide reacts rapidly with atmospheric oxygen and is oxidized to form the dioxide. This exothermic reaction requires a very small activation energy and takes place easily even at room temperature (see §9, Chapter VI). Thus, the chemical processes in heated and subsequently cooled air lead to a state substantially out of equilibrium. This result is in sharp contradiction with the laws of chemical equilibrium, according to which the oxides of nitrogen at low temperatures should be completely transformed into nitrogen and oxygen. This effect, well known in laboratory practice, is called the effect of "freezing" of the oxides of nitrogen.

A large amount of nitrogen oxides is formed in a strong explosion in air. The atmospheric nitrogen is oxidized at that stage of the process when the air in the explosion wave is heated to a temperature of several thousand degrees, at which stage a few percent of the nitrogen is oxidized. As the explosion wave is propagated, the air initially heated by the shock front is cooled very rapidly. The nitric oxide which was formed does not have sufficient time to decompose on cooling, and remains in the air "forever." The total weight of oxides of nitrogen which is formed in air during an explosion with an energy of \( 10^{21} \) erg, equivalent to approximately 20,000 tons of TNT, is 100 tons. Several tens of seconds or a minute after the detonation all of the oxide has been transformed into the dioxide.

In its ordinary state nitrogen dioxide is a strongly colored brownish-red gas; this is caused by the preferential absorption of green and blue light by the \( \text{NO}_2 \) molecules. It imparts the reddish hue to the cloud which rises after the explosion*. This effect has been observed experimentally and is described in [12]; see also §5 of Chapter IX. The presence of the oxides and in particular of small amounts of nitrogen dioxide in the high-temperature air encompassed by an explosion wave has a strong effect on the optical properties of the air behind the wave, since, unlike oxygen and nitrogen molecules, the molecules of the dioxide intensely absorb and emit light in the visible part of the spectrum (the NO molecule also does not absorb visible light).

The specific features of the chemical kinetics for the formation and decom-

* The molecular complexes \( \text{N}_2\text{O}_4 \) do not absorb visible light, so that the \( \text{N}_2\text{O}_4 \) gas is colorless. However, the dioxide disappears only after the explosion cloud dissipates in the atmosphere, since the reaction \( 2\text{NO}_2 \rightarrow \text{N}_2\text{O}_4 \) does not proceed too rapidly.
position of nitrogen oxides in an explosion wave give rise to interesting optical phenomena observed in a strong explosion, a description of which may also be found in [12]. These phenomena are: luminosity of the shock wave at comparatively low temperatures, of the order of 4000—2000°K behind the front, at which the gas, consisting of oxygen and nitrogen atoms only, should not be incandescent; a rather sudden cut-off of the shock wave luminosity at a temperature of about 2000°K, and the separation of the shock wave from the boundary of a glowing body, the so-called “fireball”; the distinctive effect of a minimum in the brightness of the fireball at the instant of separation, when the glow starts to die down and after which the ball again flares up. These effects will be considered in §§5–7 of Chapter IX. Here, we shall consider in more detail the kinetics of the nitrogen oxidation reaction in an explosion wave; these considerations are necessary to explain the above optical phenomena. This problem was considered by one of the present authors [13]. It should be pointed out that the study of the kinetics is in itself very interesting, since it provides a characteristic example of a chemical process substantially out of equilibrium within the gasdynamic phenomenon of a strong explosion.

The gasdynamics of a strong explosion was described in §25 of Chapter I. The process is self-similar, the shock front is propagated from the explosion center as \( R_f \sim t^{2/5} \). The distributions of all the flow variables with respect to radius are given in Fig. 1.50. These distributions do not change with time, because the process is self-similar; only the scales are time dependent.

Of interest to us here is the course of the chemical reaction in specific parcels of air. For this it is first necessary to know how the thermodynamic state of a given parcel changes with time. The \( r, t \) diagram of Fig. 8.6 shows

![Fig. 8.6. An \( r, t \) diagram for a strong explosion in air. \( f \) is the trace of the shock front; 1, 2, and 3 are the traces of three parcels over which the front passes at the times \( t_{01}, t_{02}, \) and \( t_{03} \).](image)

schematically the trace of the shock front path, and of several of the particle paths behind the front, denoted by the numbers 1, 2, and 3. The parcels which are heated and compressed at the times \( t_{01}, t_{02}, \) and \( t_{03} \) when the wave front passes them are carried away suddenly by the explosion wave from the center and in the process are isentropically expanded and cooled until the
§5. Oxidation of nitrogen in strong explosions in air

pressure decreases to atmospheric and the parcels stop moving. The expansion and cooling curves for the air parcels as a function of time are shown schematically in Figs. 8.7 and 8.8.

Fig. 8.7. Schematic time dependence of the temperature in three parcels heated by an explosion wave.

Fig. 8.8. Schematic time dependence of the density in three parcels compressed by an explosion wave.

Calculations carried out with the formulas of §25 of Chapter I show that in an explosion with an energy \( E = 10^{21} \text{ erg} \), (this value will be used in all our numerical examples), the temperature at the shock front decreases to \( T_f = 2000^\circ \text{K} \) in a time of the order of \( 10^{-2} \text{ sec} \) from the moment of energy release. The times for cooling the air parcels from a temperature of, let us say, \( 5000^\circ \text{K} \) to \( 2000-1500^\circ \text{K} \) are of the same order. The time \( t \sim 10^{-2} \text{ sec} \) is thus a time scale for the gasdynamic process in an explosion with an energy \( E = 10^{21} \text{ erg} \), to which the characteristic times for the chemical reactions should be compared.

Let us first follow the reaction kinetics in a particular parcel of air. Let, for example, parcel 1 be heated by the shock front to a temperature \( T_{f1} = 3000^\circ \text{K} \). The rate of nitrogen oxidation at this temperature is very high and the equilibrium concentration is reached in a time of the order of \( 10^{-6} \text{ sec} \). Approximately 5% of the nitrogen in the parcel of air is oxidized "instantaneously", after which the concentration of the oxide slowly changes (decreases) in accordance with the laws of chemical equilibrium, following the cooling and expansion. The decomposition of the oxide molecules begins to lag behind the cooling only when the parcel is cooled down to a temperature of the order of \( 2300^\circ \text{K} \), at which the relaxation time \( \tau \) has increased from the initially small value of \( \sim 10^{-6} \text{ sec} \) to a value comparable to the gasdynamic time scale for cooling, i.e., \( 10^{-2} \text{ sec} \). On further cooling the decomposition stops abruptly, since the decomposition rate drops very
rapidly with decreasing temperature. Thus, already at a temperature of 2000°K the decomposition rate is characterized by a relaxation time \( \tau \sim 1 \text{ sec} \). The residual frozen amount of the oxide in the given parcel corresponds approximately to that concentration which existed at the time when the relaxation time \( \tau \) was comparable with the characteristic cooling time \( \tau \sim 10^{-2} \text{ sec} \), when the temperature in the parcel was of the order of 2300°K. However, slightly earlier the concentration was in equilibrium, and the equilibrium concentration changes only very weakly when the temperature is decreased by several hundred degrees; such a drop in temperature, however, appreciably changes the decomposition rate (see §4, Chapter III, and §8, Chapter VI). Hence, the residual concentration of the oxide in the air parcel is simply equal to the equilibrium concentration at a temperature of about 2300°K, and this is a quantity of the order of 1%. The time dependence of the oxide concentration in the parcel is shown schematically in Fig. 8.9. Of course, the exact value of the residual concentration depends on the particular parcel, in particular on the density with which it arrived at the critical reaction temperature (for this reaction \( \approx 2300°K \)) at which \( \tau \sim t \), as well as on the cooling time. These details, however, do not affect the order of magnitude of the residual concentration. The oxidation of the oxide to the dioxide at temperatures of \( \sim 2000°K \) proceeds quite rapidly (see §9, Chapter VI). Therefore, the concentration of the dioxide corresponds to equilibrium, but the dioxide is in this case in equilibrium with the actual frozen amount of the oxide and not with the equilibrium amount of the oxide. At temperatures of the order of 2000°K the concentration of the dioxide is approximately 0.01% (see Table 5.9 in §21 of Chapter V). Subsequently, the entire oxide is gradually oxidized to the dioxide; here the process at first follows the cooling, and then, at temperatures of \( \sim 1500°K \) and below, it lags behind the cooling. Total oxidation of the oxide is completed when the parcel is quite cold, some tens of seconds after the explosion.

In air parcels which were heated by the shock front to temperatures below \( \sim 2200-2000°K \), in general, no nitric oxide is formed at all, since the oxidation rate at such temperatures is very low, and the parcel quickly passes through the temperature region of approximately 2000°K in which the reac-
§5. Oxidation of nitrogen in strong explosions in air

Oxidation rate is still appreciable. Thus, a spherical air layer, heated by a shock front to a temperature of \( \sim 2200\text{--}2000\,\text{°K} \), limits, in general, the mass of air in which the oxide and then the dioxide have appeared (the motion of this layer is described on the \( r, t \) diagram of Fig. 8.6, say, by the trace 3). From this, we also get the estimate of the total amount of oxides of nitrogen formed in a strong explosion. This amount is determined by the mass of air heated by the shock front to a temperature above \( \sim 2200\text{--}2000\,\text{°K} \), and by the equilibrium concentration of the oxide at this temperature (actually, at a slightly higher temperature—\( 2300\,\text{°K} \)), since the freezing takes place particularly at these temperatures*. In an explosion with an energy of \( 10^{21}\,\text{erg} \) the radius of the shock front at a front temperature \( T_f = 2000\,\text{°K} \) is approximately 100 m. The mass of air in a spherical volume of this radius is approximately 5000 tons, and at a concentration of \( \sim 1\% \) the mass of the oxide is \( \sim 50 \) tons. The mass of the dioxide, upon addition of still another oxygen atom to each NO molecule, is \( \sim 75 \) tons, that is, about 100 tons as was stated previously.

Let us now consider the distribution of the concentration of oxides with respect to the radius at a given instant of time. Two typical cases are possible. If at the time \( t' \) (Fig. 8.10) the temperature at the wave front is above \( \sim 2300\,\text{°K} \), then for practically all the parcels behind the front the concentrations of the oxide and dioxide are equal to their equilibrium values and the distributions of the concentrations are simply determined by the temperature and density distributions behind the front. The only exception is a very thin layer of air immediately behind the front, in which the oxides at this time have not yet formed (Fig. 8.10).

If we consider now the time \( t'' \), when the temperature behind the front is less than \( \sim 2000\,\text{°K} \), for example 1600°K, then we find in the vicinity of the front parcels which have been heated by the front to temperatures below

\* We recall that the equilibrium concentration of nitric oxide in air depends only on the temperature, and not on the density (see §4, Chapter III, and §8, Chapter VI).
2000°K; in general, this gas does not contain any oxide. Far from the front, at temperatures above ~2500°K, the concentration is at its equilibrium value, while in an intermediate layer the oxide is present, but not in its equilibrium concentration. Closer to the front it is lower than its equilibrium value, and slightly farther away, in those parcels in which freezing has already begun, it is higher than at equilibrium (Fig. 8.11).

In order to calculate the concentration of the oxide in the nonequilibrium region, and also to determine more precisely the amount of frozen oxide, we must solve the rate equation (6.45) for the oxidation of nitrogen in the given parcel of air, taking into account the relationships governing the cooling and expansion behind the explosion wave. The relationships governing the expansion and cooling of air, which follow from the solution of the problem of a strong explosion (§25, Chapter I), can be well approximated by the following equations, which are convenient for use in rate calculations

\[ \rho = \rho_0 \left( \frac{t_0}{t} \right)^{2b} \]

\[ \frac{1}{T} = \frac{1}{T_0} + \frac{a}{T_0} \ln \frac{t}{t_0} \]

Here \( T_0 \) and \( \rho_0 \) are the temperature and density in the parcel at the initial time \( t_0 \), when the shock front passed through it, and \( a \) and \( b \) are numerical constants, depending only on the effective specific heat ratio in the gasdynamic solution. For \( \gamma = 1.30 \), \( a = 0.44 \) and \( b = 0.75 \).

It has been shown (see [13]) that by an appropriate choice of new variables in the rate equation (6.45) this equation, together with the known relations...
the cooling and expansion, can be reduced to the universal dimensionless form

$$\frac{dy}{dx} = x^{3-\delta}(y^2 - x^2).$$

(8.24)

Here the quantity \(x\) is related to the time variable, \(y\) is proportional to the oxide concentration, and \(\delta\) is a numerical constant less than unity. The initial condition corresponding to the absence of oxide at the initial time \(t = t_0\) reduces to the condition \(y = 0\), with \(x\) equal to some value \(x_0\) which depends only on the time \(t_0\), the initial values of the state variables, and on the constants entering the rate equation (6.45). Zel'dovich, Sadovnikov, and Frank-Kamenetskiii [14] have studied the kinetics of the nitrogen oxidation reaction under laboratory conditions with a cooling law of the type \(1/T = (1/T_0) + (a'/T_0)t\), at constant density. With new variables introduced, the rate equation (6.45) was also reduced to an equation of the type (8.24) with the initial condition \(y = 0\) when \(x = x_0\). Reference [14] gives a tabulation of the solution of the equation \(y = y(x, x_0)\).

Knowing the initial state variables for an air parcel from the gasdynamic solution of the problem of a strong explosion, we can thus obtain a complete solution of the dependence of the oxide concentration \(c_{NO}\) on time. This solution is in complete agreement with the qualitative considerations presented above. The curve presented in Fig. 8.11 was calculated in this manner.

3. Disturbance of thermodynamic equilibrium in the sudden expansion of a gas into vacuum

§6. Sudden expansion of a gas cloud

The phenomenon of sudden expansion of a gas cloud into vacuum is encountered in various natural, laboratory, and industrial processes. Meteorite impacts on planet surfaces result in the sudden braking of the meteorites and the conversion of their kinetic energy into heat. If the impact velocity is high, of the order of several tens of kilometers per second, very high temperatures result, of the order of tens or hundreds of thousands of degrees. The meteorite and a part of the planet soil are vaporized during the impact. This phenomenon resembles a strong explosion on the planet's surface†. If the

* As was noted by Kompaneets, the equation (8.24) with \(\delta = 0\) can be solved exactly in terms of Bessel functions.
† The hydrodynamics of this process will be considered in Chapter XII.
planet is without an atmosphere (as for example in the case of the moon) the vapor cloud generated, with tremendous expansion velocities, overcomes the force of gravity and freely expands into vacuum. A hypothesis has been advanced that the lunar craters were formed as a result of such “explosions” from the impacts of extremely large meteorites. Similar phenomena also take place in the much more frequent collisions between small bodies in the solar system—the asteroids.

Sudden expansion into vacuum of tremendously large gas clouds is observed during nova outbursts, in which a disturbance in the energy balance of the star leads to the release of a large amount of energy and a shock wave is propagated from the central layers to the periphery. This shock wave separates from the surface of the star and emits a gas cloud into space. To some extent, similar phenomena (but on very much smaller scale) are also encountered under laboratory conditions. An example is the vaporization of the anode needle of a pulsed x-ray tube caused by a strong electron discharge (Tsukerman and Manakova [15]); another is the explosion of wires by electric currents in vacuum systems. Of course, the expansion under laboratory conditions is not unbounded since it is bounded by the walls of the vacuum chamber; however, at the stage when the gas has not yet reached the walls, the expansion into the vacuum takes place in the same manner as if the vacuum were “infinite”.

Experiments in which a gas cloud suddenly expands into a vacuum were also carried out in connection with rocket probe studies of the upper layers of the atmosphere when sodium vapor and nitric oxide were released into space. The same phenomenon also occurred when an artificial comet was created during the moon flight of the Soviet cosmic rocket.

The dynamics of the sudden expansion of a gas cloud into vacuum is very simple; an idealized problem of the sudden isentropic expansion of a gas sphere into vacuum, for a gas with constant specific heats, was considered in §§28 and 29 of Chapter I. Here we shall be interested in certain fine points concerning the state of the gas during the later stage of the expansion to infinity, when the expansion can be treated on the basis of a very simple scheme. In this scheme we shall consider the behavior of only the mass-averaged flow variables. It is clear that the variables describing any particular gas particle change with time in exactly the same manner as do the averaged quantities and differ from the average values only by numerical factors which are of the order of unity and which are not of great importance for our purpose.

Let us consider a gas sphere of mass \( M \) and energy \( E^* \). Almost the entire initial energy has been transformed into kinetic energy during the earlier

* For convenience, we shall repeat here some of the results of §28, Chapter I.
phase of the expansion, and the fluid expands by inertia with the average velocity
\[ u = \left( \frac{2E}{M} \right)^{1/2}. \]

The sphere radius is of the order of \( R = ut \) and the gas density decreases with time according to the relation
\[ \rho = \frac{M}{4\pi R^3/3} = \rho_0 \left( \frac{t_0}{t} \right)^3, \quad (8.25) \]
where the characteristic time scale is approximately expressed in terms of the initial radius of the sphere \( R_0 \) and the initial fluid density \( \rho_0 \) by
\[ t_0 = \left( \frac{M}{\rho_0 4\pi u^3/3} \right)^{1/3} = \frac{R_0}{u}. \quad (8.26) \]

If we are interested in the gas temperature during the later stage of the expansion, we must consider the small amount of internal energy that still remains in the gas, which we neglected in calculating the expansion velocity. We take into account the fact that the specific entropy of the gas \( S \) remains constant during the expansion. Assuming for simplicity that the fluid behaves as a gas with some constant effective value of the specific heat ratio we obtain for the cooling of the gas the relation
\[ T = A(S) \rho^{\gamma-1} \sim t^{-3(\gamma-1)}, \quad (8.27) \]
where \( A(S) \) is a constant which depends on the entropy and which can be calculated from the well-known formulas of statistical mechanics and thermodynamics. If we consider relatively high temperatures then, taking into account the processes of ionization, dissociation, etc., we can take as an approximate value for the specific heat ratio \( \gamma \approx 1.2-1.3 \). In any case, the ratio is not greater than \( 5/3 = 1.66 \), which corresponds to a complete freezing of all the internal degrees of freedom in the gas.

§7. Freezing effect

Let us consider the physical and chemical processes taking place in a gas expanding according to the cubic relation \( \rho \sim t^{-3} \) and cooling as \( T \sim t^{-3(\gamma-1)} \). We assume that the initial temperature was high, so that the molecules were dissociated and the atoms strongly ionized. We further assume that the initial density of the gas was also high, as is usually the case when a gas cloud is formed by the rapid release of energy in an initially solid substance. Then, during the early stage of the sudden expansion, at high density and temperature, all relaxation processes proceed very rapidly and the gas remains in
thermodynamic equilibrium; the characteristic state variables of the gas, as for example the degrees of ionization or dissociation, follow the expansion and cooling. If during the entire expansion the gas were to remain in thermodynamic equilibrium, then in the process of expansion and cooling all the electrons would rather quickly combine with the ions into neutral atoms, and all the atoms with a chemical affinity would combine into molecules.

Actually, the equilibrium degrees of ionization and dissociation have an exponential dependence on temperature but only a power-law dependence on the density: \( \alpha \sim \rho^{-1/2} \exp(-I/2kT) \), where \( I \) is the ionization potential or dissociation energy. For an expansion with cooling to low temperatures, the equilibrium degrees of ionization and dissociation rapidly approach zero, since as \( T \sim \rho^{-1} \to 0 \) the exponential term decreases extremely rapidly, much more rapidly than the preexponential factor increases. It can be easily seen, however, that no matter how high the initial rate of establishment of thermodynamic equilibrium in comparison with the cooling and expansion rates, there is a time at which the ratio of these rates will be reversed, thermodynamic equilibrium will no longer be established, and the degrees of ionization and dissociation will begin to depart increasingly from their equilibrium values.

In fact, the equilibrium degrees of ionization and dissociation are established as a result of the mutual compensation of the direct and reverse processes. But at low temperatures the ionization and dissociation, which require large expenditures of energy, drop very sharply. The rates of these processes depend on temperature as \( \exp(-I/kT) \), and for \( kT \ll I \) they depend extremely strongly on temperature, and thus on time. On the other hand the rates of the reverse recombination processes have only a power-law dependence on density and temperature and consequently on time. Thus, ionization and dissociation will essentially stop at a certain instant, after which the degrees of ionization and dissociation will decrease with time following a power law, while the equilibrium values drop exponentially.

The rates of recombination processes decrease as a result of an expansion, and recombination may cease entirely. We can convince ourselves of this by taking as an example the recombination of atoms into molecules (recombination of electrons with ions will be considered in the following sections). Recombination at high densities takes place by three-body collisions, while two-body collisions are responsible for recombination at low densities, so that it is sufficient to consider the latter in the later stage of the expansion. Let \( N \) be the number density, \( \bar{v} \sim \sqrt{T} \) the thermal speed, and \( \sigma \) the recombination cross section, which is no larger than the gaskinetic cross section. The recombination rate \( dN/dt = -N\bar{v}\sigma \) and the characteristic time during which appreciable changes take place in the degree of dissociation is \( \tau \approx 1/N\bar{v}\sigma \). Even if we do not take into account the decrease in the number of atoms as a
result of recombination, the atom number density $N$ will decrease in proportion to $1/t^3$ as a result of the expansion of the gas, $\bar{n} \sim \sqrt{T} \sim t^{-\frac{3}{2} \left(\frac{\gamma - 1}{\gamma} - 1\right)}$ so that $\tau \sim t^{3+\frac{2}{\gamma-1}} = t^{\frac{2}{\gamma} (\gamma - 1)}$, and the characteristic time $\tau$ increases faster than $t$; consequently, at some instant of time it will become greater than $t$. On the other hand, the time scale characterizing the changes in density and temperature is the time $t$ itself, measured from the beginning of the sudden expansion, since $dT/dt \sim -T/t$ and $dp/dt \sim -\rho/t$. Thus, at some time recombination begins to lag ever increasingly behind the cooling. Moreover, beginning approximately at this time, the probability of recombination of the given atom with all other atoms during the remaining expansion to infinity is less than unity; in other words, the recombination does not proceed to completion. In fact, this probability is equal to

$$w = \int_{t_1}^{\infty} N\bar{n} \sigma \, dt = \int_{t_1}^{\infty} \frac{1}{\tau} \int_{t_1}^{\infty} \left(\frac{t_1}{t}\right)^{\frac{2}{\gamma} (\gamma - 1)} \, dt \approx \frac{t_1}{\tau_1} = \text{const.} \quad (8.28)$$

Starting at the time $t_1$ at which $\tau_1 > t_1$, the recombination probability of a given atom $w < 1$. Thus, the gas expands to infinity in the dissociated state. This phenomenon is called “freezing” of the atoms.

Starting at some time, the gaskinetic collisions in the gas also cease almost entirely. Deexcitation of the vibrational and rotational modes of molecular excitation by particle collisions stops. This follows from the convergence of the same collision integral (8.28). However, freezing of the molecular vibrational and rotational modes does not take place; the vibrational and rotational energies of the molecules are carried away by the spontaneous emission of photons. The vibrational transitions produce radiation in the infrared region of the spectrum and the rotational transitions result in the emission of radio frequencies.

Owing to the convergence of the collision integral when the gaskinetic cross section (for the neutral atoms) is substituted, the exchange of energy of the random translational motion of the atoms also ceases after a certain time in a spherical sudden expansion. The remainder of the expansion then continues without collisions*. All of the particles move by inertia with the velocity which they have acquired in their last collision. In this case the particles, in general, have a nonradial ("random") velocity component. It would seem that “freezing” of the random velocity, that is, “temperature”, should take place. Actually, as was noted by Belokon’ [16], this does not happen for purely geometrical reasons. The problem consists in the definition of the concepts of hydrodynamic and internal energy when particle collisions are

* It is interesting to note that for a sudden expansion with $\gamma = 5/3$ the frequency of Coulomb collisions of charged particles does not decrease, since $\sigma \sim T^{-2}$ and $N\bar{n} \sigma \sim NT^{-3/2} \sim N^{5/2 - 3\gamma/2} = \text{const.}$. 

§7. Freezing effect
absent. The internal energy of a unit volume of gas is equal to the difference between the total kinetic energy \( \frac{1}{2} N m \bar{v}^2 \) (\( N \) is the number of particles per unit volume, \( m \) their mass, and \( \bar{v}^2 \) the mean square velocity) and the kinetic energy of “hydrodynamic” motion \( \frac{1}{2} N m (\bar{v})^2 \), where \( (\bar{v})^2 \) is the square of the mean velocity:

\[
E_{\text{int}} = E_{\text{total}} - E_{\text{hydrod}} = \frac{1}{2} N m (\bar{v}^2 - (\bar{v})^2).
\]

Let us suppose that the collisions stop at a time \( t_1 \), when the gas occupies a sphere of radius \( r_1 \) (Fig. 8.12). Particles leaving the sphere arrive at points \( A \) and \( B \) at times \( t' \) and \( t'' \) with velocities whose directions are included within the cones shown in Fig. 8.12. It is clear that the greater is the distance from the center, the narrower is the cone and the closer \( \bar{v}^2 \) is to \( (\bar{v})^2 \), the smaller is the difference \( \bar{v}^2 - (\bar{v})^2 \). In the limit \( t \to \infty, r \to \infty \) all particles move in an exactly radial direction. In this limit \( \bar{v}^2 = (\bar{v})^2 \), and the entire translational internal energy has been transformed into hydrodynamic energy*.

In cylindrical and planar sudden expansions, thermodynamic equilibrium is also definitely disturbed, but of course the changes with time in the degrees of dissociation and ionization follow different laws. It should be noted that, if the mass of the gas is finite, then, when the gas has undergone a sufficiently

* Editors’ note. Besides the geometrical effect, another effect must be invoked for this conclusion. The particle velocities at the point \( A \) are not uniform in magnitude, but lie between \( (r' - r_i)/(t' - t_i) \) and \( (r' + r_i)/(t' - t_i) \). With \( t' \) very large the variation in particle velocity is of the order of \( r_i/t' \). In the limit \( t \to \infty, r \to \infty \) this variation approaches zero, so that the particle velocities approach uniformity in magnitude as well as in direction. In this limit, then, \( \bar{v}^2 = (\bar{v})^2 \).
large expansion, cases which are initially planar or cylindrical must become spherical cases.

We note a number of other papers [15a, 24–26] devoted to various problems of the free molecular sudden expansion of a gas into a vacuum without collisions (these articles also contain references to other papers). Reference [27] considers the sudden expansion of an ionized gas into a vacuum in which there is a magnetic field.

§8. Disturbance of ionization equilibrium

We now consider in more detail the problem of the disturbance of ionization equilibrium resulting from the expansion of a gas, and show how we can establish approximately the time at which the equilibrium is disturbed (the method presented below was suggested by one of the authors [17]). We assume that initially the gas temperature was high and the atoms were multiply ionized. As the expanding gas cools, electrons are reseated at the appropriate levels in the atoms, and the degree of ionization decreases. Let the ionization equilibrium be disturbed only during the later stage of a sufficiently strong expansion and cooling, when it is the last electrons which are reseated in the atoms, i.e., when the process taking place is the reverse of single ionization of the atoms. The gas at this time is essentially expanding by inertia, with the speed constant and the density changing as $1/t^3$.

The mechanism of recombination of ions and electrons was considered in detail in Chapter VI. The electrons are captured by ions in three-body collisions with an electron acting as the third body; at temperatures which are not too high the electrons, as a rule, are captured into the upper levels of the atoms. Captures by two-body collisions with the emission of a photon are also possible (in this case the electrons are primarily captured into the ground level). Such photorecombination is of importance only at very low electron densities $N_e \text{ cm}^{-3}$. The lower the temperature the lower must be the electron density for photorecombination to be important. According to (6.107) this process predominates only under the condition that $N_e < 3.1 \cdot 10^{13} T_e^{3.75} = 3.2 \cdot 10^9 T_{\text{thous. deg}}^{3.75}$. However, in the majority of cases of sudden expansion which are of interest, at the stage when equilibrium is disturbed at temperatures of several thousand degrees, the electron density is much higher and photorecombination plays no role, neither at the time when the equilibrium is disturbed nor later.

If when the gas is still close to equilibrium the main role is played by recombination from three-body collisions, then ionization takes place as a result of the reverse process, that of the removal of electrons primarily from excited atoms by free electron impact. According to the detailed balancing principle, the ionization rate can be expressed in terms of the recombination
coefficient and the equilibrium constant or the equilibrium degree of ionization. In this case the rate equation for the degree of ionization $x = N_e/N$ ($N$ is the number of nuclei, atoms plus ions per unit volume) is expressed in the form

$$\frac{dx}{dt} = bN(x_{eq}^2 - x^2). \quad (8.29)$$

Here $b$ is the recombination coefficient which, at not too high temperatures, not above several thousand degrees, is given by (6.106)

$$b = \frac{ANx}{T^{9/2}}, \quad (8.30)$$

$$A = 8.75 \times 10^{-27} \text{ cm}^6 \cdot \text{ev}^{9/2} / \text{sec} = 5.2 \times 10^{-23} \text{ cm}^6 \cdot \text{(thousand deg)}^{9/2} / \text{sec}.$$  

Here $x_{eq}$ is the equilibrium degree of ionization given by the Saha equation. For values of $x_{eq}$ not large in comparison with one we have, approximately,

$$x_{eq} \approx 7 \times 10^7 \left(\frac{g_T}{g_a} \frac{T_0^{3/2}}{N} \right)^{1/2} e^{-3/2kT} \quad (8.31)$$

When the expansion and cooling are governed by the known relations in which $N(t)$ and $T(t)$ are given by (8.25) and (8.27), then (8.29) becomes an ordinary differential equation for the desired function $x(t)$. Since we are primarily interested in the qualitative features of the problem, we shall solve this equation only approximately. The initial ionization and recombination rates, which are proportional to the terms on the right-hand side of (8.29), are large in comparison with the expansion and cooling rates. (For the purpose of comparing rates of the different processes we shall use relative rates expressed in reciprocal seconds, for example, $T^{-1}dT/dt$ and $N^{-1}dN/dt$). Ionization and recombination almost completely cancel each other; the degree of ionization follows the expansion and cooling and remains close to its equilibrium value. Approximately, $x(t) \approx x_{eq}(t) \equiv x_{eq}[T(t), N(t)]$ and the difference $|x_{eq}^2 - x^2| \ll x_{eq}^2$.

The small departure of the degree of ionization from its equilibrium value which inevitably exists (since the temperature and density change with time) can be approximately estimated by setting $dx/dt \approx dx_{eq}/dt$ on the left-hand side of (8.29), replacing $x$ in the expression for the recombination coefficient by $x_{eq}$, and setting $x_{eq}^2 - x^2 \approx 2x_{eq}(x_{eq} - x)$. It can be easily checked that the relative departure $|x_{eq} - x|/x_{eq}$ increases with time (since the rate of the relaxation process becomes increasingly lower in comparison with the rate of change of the macroscopic parameters temperature and density).

Ionization equilibrium is appreciably disturbed when the difference between the ionization and recombination rates increases to a value of the order of
§9. Recombination following disturbance of ionization equilibrium

the rates themselves, that is, when the quantity $|x_{eq}^2 - x^2|$ becomes of the order of $x_{eq}^2$. To estimate the time $t_1$ when the equilibrium is disturbed and the values of $T_1, N_1,$ and $x_1$ at this time, we can again set $dx/dt \approx dx_{eq}/dt$ and $x \approx x_{eq}$ in the recombination coefficient, and equate the difference $x^2 - x_{eq}^2$ to the value of $x_{eq}^2$. Differentiating with respect to time the equilibrium degree of ionization given by (8.31), taking into account the fact that the most rapidly changing factor is the exponential Boltzmann factor, and then using the cooling relation (8.27) (which yields $dT/dt = -3(y - 1)T/\gamma$), we find an equation which determines the time when the equilibrium is disturbed:

$$b_1N_1x_{eq}t_1 = \frac{3}{k}T_1. \quad (8.32)$$

Here $b_1 = b(T_1, N_1, x_{eq})$. This equation, together with the expansion and cooling expressions (8.25), (8.27), and the Saha equation (8.31) referred to the time $t_1$, reduce to a transcendental equation for the temperature $T_1$. Having found $T_1$, it is easy to calculate the remaining quantities $t_1, N_1,$ and $x_{eq}$. (Within the approximation used we can take the actual degree of ionization $x_1$ equal to the equilibrium value $x_{eq}$.)

§9. The kinetics of recombination and cooling of the gas following the disturbance of ionization equilibrium*

After the equilibrium is disturbed the ionization rate, which is proportional to $x_{eq}^2$, continues to decrease rapidly with time according to the exponential relation $e^{-1/kT(t)}$. The recombination rate, which is proportional to the square of the actual degree of ionization, decreases much more slowly and soon becomes appreciably larger than the ionization rate: $x(t) > x_{eq}(t)$. Under these conditions it is possible to neglect ionization and to assume that only recombination takes place. The rate equation (8.29) will then be approximately written as

$$\frac{dx}{dt} = -bNx^2 \quad \text{for} \quad t > t_1. \quad (8.33)$$

If the recombination coefficient $b$ were entirely independent or only weakly dependent on the temperature, then, as a result of the rapid decrease in density, the recombination rate would have dropped and recombination would soon have stopped entirely. This is precisely the situation that takes place with the recombination of atoms into a molecule (see §7). On the other hand, in our case the recombination coefficient (8.30) is very temperature sensitive ($b \sim T^{-9/2}$), and the decrease in the recombination rate due

* This section is based on a paper by Kuznetsov and one of the authors [28].
to the drop in density in the expanding gas is compensated to an appreciable extent by the increase in the recombination rate coefficient due to cooling. For this reason particular importance is attached to the question of the relation governing the temperature decrease with time. In fact, let us write the formal solution of the differential equation (8.33) using the recombination coefficient (8.30),

\[ x = \frac{x_1'}{\left[1 + 2A x_1' \int_{t_1'}^t N^2 T^{-9/2} \, dt\right]^{1/2}}. \quad (8.34) \]

Here the values of \( t_1' \) and \( x_1' \) are determined from initial conditions (to the order of this approximation we may require that the integral curve \( x(t) \) pass through the point where the equilibrium is disturbed, so that \( t_1' = t_1 \) and \( x_1' = x_1 \)). We shall, as previously, characterize the temperature drop with time by the power-law behavior \( T \sim t^{-m} \); the quantity \( N \sim t^{-3} \).

According to (8.34) the asymptotic behavior of the degree of ionization depends to a large extent on the cooling rate, that is, on the value of the exponent \( m \). If the gas is cooled "slowly" and \( m < 10/9 \) (which corresponds to a specific heat ratio \( \gamma = 1 + m/3 < 1.37 \)) the integral in (8.34) converges for \( t \to \infty \) and the degree of ionization approaches a constant value different from zero, so that recombination does not go to completion. However, if the gas is cooled "rapidly" and \( m > 10/9 \), the integral diverges for \( t \to \infty \) and the degree of ionization tends to zero, following \( x \sim t^{-(9/4)(m-10/9)} \). For \( m = 10/9 \) it also goes to zero, but logarithmically, following \( x \sim (\ln t)^{-1/2} \).

Thus for \( m \geq 10/9 \) the electrons and ions must eventually recombine.

But the rate of cooling of the gas itself depends on the mode of recombination, since the recombination releases the potential energy of the free electrons previously removed from the atoms, and this energy is partially transformed into heat. Consequently, in order to solve for the behavior of the degree of ionization with time we must consider together the kinetics of the recombination and the balance of thermal energy in the gas.

In the recombination of an electron in a three-body collision the electron is first captured by the ion into one of the upper levels of the atom with a binding energy \( E \) of the order of \( kT \) (see Chapter VI). Then, under the action of electron collisions of the second kind but also as a result of spontaneous radiative transitions, the bound electron descends down the energy levels of the atom to the ground level. The process of deexcitation of an excited atom usually takes place rapidly in comparison with the rates of electron capture by ions and of the change in gas temperature. For this reason we may assume approximately that the excited atom which is formed is deexcited immediately following capture, and the potential energy \( I \) from the recombination is immediately transformed into other forms of energy. A part \( E^* \) of it is transferred directly to the free electrons by the electron collisions of the second
§9. Recombination following disturbance of ionization equilibrium

kind (and then is distributed over the entire gas as a result of energy transfer between the electrons and ions). The other part of the binding energy $I - E^*$ that is released as a result of radiative transitions is first transformed into line radiation. This radiation in part leaves the gas volume and in part is absorbed by atoms, where the absorption is principally that of the resonance radiation corresponding to the transition of the excited atom directly to the ground state. Through absorption of a resonant photon the atom becomes excited; then it re-emits, the new photon is absorbed by other atoms, etc., this process repeating itself until the photon leaves the gas volume. A so-called diffusion of resonance radiation takes place. During the diffusion of the photon the excited atom can be subjected to a collision of the second kind and give off excitation energy in the form of heat. As a result, some portion of the binding energy $I - E^*$ which was first converted into radiation will with time also be transformed into heat. This part will be less the more transparent is the gas, that is, the shorter the duration of the diffusion of resonance radiation.

We assume for simplicity that the energy $I - E^*$ is completely lost by the gas (corresponding to a transparent gas volume). This assumption underestimates the heat release in the gas and tends to underestimate the temperature; the calculation of the recombination kinetics for this condition will lead to an underestimate of the degree of ionization, and thus yields a lower limit. The above assumption is more justified the more transparent is the gas, and thus the later is the stage of the expansion which we consider. Hence the assumption is valid asymptotically.

In setting up the equation of the energy balance for the gas we shall assume for simplicity that the electron and ion (atom) temperatures are the same. Estimates indicate that in the majority of cases, even after a considerable length of time has passed since the ionization equilibrium was first disturbed, the energy transfer between the electron and ion gases takes place rapidly and the temperatures of these gases are close to each other*. Let us write the energy equation for the gas per heavy particle (per original atom). The thermal energy is $\varepsilon = \frac{3}{2}(1 + x)kT$, the specific volume $V = 1/N$, and the gas pressure $p = N(1 + x)kT$. Then

$$\frac{ds}{dt} + p \frac{dV}{dt} = E^* \left( -\frac{dx}{dt} \right). \quad (8.35)$$

From this, using the relation for the expansion $N \sim t^{-3}$, we obtain the equation for the temperature

$$\frac{dT}{dt} + 2 \frac{T}{t} = \frac{3E^*/k + T}{1 + x} \left( -\frac{dx}{dt} \right). \quad (8.36)$$

* In [28] the equations were set up taking differences between the electron and ion temperatures into account.
To calculate the heat release per recombination $E^*$ we consider the process of the deexcitation of the excited atom which is formed as the result of the capture of an electron by an ion. As noted above, in three-body collisions the electron is, as a rule, captured into one of the very high atomic levels with a binding energy $E \sim kT$. The distances between levels in this region are much less than $kT$. In collisions with free electrons the bound electron in the excited atom moves to neighboring levels with transitions “upward” and “downward” almost equally probable, so that the change in the energy of an excited atom under the action of electron impacts has the character of a diffusion along the energy axis; on recombination the diffusive flux is directed downward, in the direction of the ground state of the atom (see §18 of Chapter VI). The deexcitation rate, that is the rate of increase in the binding energy of the bound electron $dE/dt$, can be calculated by multiplying the unsteady diffusion equation (6.109) by the energy $E$ and integrating over the entire spectrum. Since we are considering an unsteady case of the motion of an electron along the energy axis $E$ from a source located in the region of low binding energies, it follows that in the region of high energies we should specify the boundary condition that the distribution function and the diffusive flux are zero. The above procedure gives an approximate expression for the rate of change of the electron binding energy

$$\frac{dE}{dt} \approx \frac{D}{kT},$$

where $D$ is the diffusion coefficient given in §18 of Chapter VI. This equation loses its validity in the region where the distance between the levels is greater than $kT$, since in this region transitions to the lower levels are significantly more probable than transitions to the upper levels, and the motion has a unidirectional character. In this region

$$\frac{dE}{dt} \approx \beta_{n,n-1} N_e \Delta E_{n,n-1},$$

where $\beta_{n,n-1} N_e$ is the transition probability from level $n$ to level $n-1$ (in sec$^{-1}$), and $\Delta E_{n,n-1}$ is the energy distance between the levels. (The expression for the rate constant of the deexcitation transition $\beta_{n,n-1}$ is given in §15, Chapter VI.)

The transition from a diffusion to a unidirectional motion of the bound electron along the energy axis takes place at a binding energy $E'$ for which the distance between levels $\Delta E_{n,n-1}$ is equal to $kT$. This energy is (for a hydrogen atom)

$$E' = \frac{1}{2} kT \left( \frac{2l}{kT} \right)^{1/3} = 2.1 \times 10^{-4} T^{2/3}.$$
As is known (see §13, Chapter V), the rate of radiative deexcitation, which is very low for low binding energies, increases rapidly as the degree of excitation decreases. After collisional deexcitation of the atom to some level radiative transitions begin to predominate. The radiation rate corresponding to the radiative transitions to neighboring levels, which determines the rate of radiative deexcitation \((dE/dt)_{rad}\), is given in §13 of Chapter V. The change from impact to radiative deexcitation takes place at a binding energy for which the rates \((dE/dt)_{impact}\) and \((dE/dt)_{rad}\) become equal. This binding energy, obviously, is the energy release \(E^*\) to be determined. It should be noted that radiative deexcitation is also promoted by radiative transitions in the atom from the upper levels directly to the ground state, after which the atom no longer interacts (see §13, Chapter V). Calculations [28] show that the contribution of this process is comparable with the contribution made by the gradual radiation which takes place with transitions to the neighboring levels.

Calculation of the heat release \(E^*\) carried out in [28] gives approximately

\[
E^* = I \times \begin{cases} 
4.3 \cdot 10^{-6} N_e^{1/3} T^{-1/2}, & \text{if } kT < E^* < E', \\
3.1 \cdot 10^{-4} N_e^{1/6} T^{-1/12}, & \text{if } E^* > E'. 
\end{cases}
\] (8.37)

After having determined the heat release \(E^*\) we can integrate the system of equations (8.33) and (8.36). As was shown in [28], the order of the system can be reduced, leading to one nonlinear differential equation of first order. Qualitative analysis of the resulting equation and of the numerical solution shows that, depending on the initial conditions, one or the other regime of the recombination process is established.

If the gas cloud expands rapidly (low cloud mass, high speed of the sudden expansion) and the ionization equilibrium is disturbed early, at a high degree of ionization with the store of potential energy of ionization in the gas greater than the thermal energy, then a large amount of heat is generated during recombination. This prevents rapid cooling of the gas and retards the recombination. Under these conditions the recombination soon ceases and the degree of ionization tends to a constant value different from zero. The electrons and ions become frozen. Practically, this happens if at the time the ionization equilibrium is disturbed all the atoms of the gas are at least singly ionized \((x_1 \geq 1)\). However, if the gas cloud expands relatively slowly

* If for any value of \(T\) and \(N_e\) we have \(E^* < kT\), this means that radiative deexcitation must start at the beginning of electron capture. This situation is usually not achieved, since in this case photorecombination dominates recombination in three-body collisions, and in photorecombination the electron is ordinarily captured into the lower, rather than into the upper atomic levels. If \(E^*\) calculated from (8.37) is found to be larger by an order of magnitude than the ionization potential \(I\), this means that the entire binding energy \(I\) is converted into heat, equation (8.37) is inapplicable, and \(E^* = I\).
(large mass, low speed of the sudden expansion) and the ionization equilibrium is disturbed late, at a low degree of ionization with the store of potential energy less than the thermal energy, the small amount of heat which is released on recombination is not capable of retarding the rapid cooling of the gas due to expansion, and the recombination rate stays sufficiently high. In this case the recombination proceeds all of the time and the degree of ionization decreases continuously, going to zero. This continues until the energy exchange between the electron and ion gases is disturbed. This happens when the characteristic exchange time $\tau_{ei}$ (see §21, Chapter VI) becomes greater than the time $t$ measured from the beginning of the expansion; this time characterizes the relative rates of expansion and cooling $V^{-1}dV/dt$ and $T^{-1}dT/dt$. After the exchange is disturbed, the heat which is released on recombination is no longer distributed uniformly among all the gas particles, but remains only in the electron gas. (The ions and atoms are cooled faster than are the electrons and their temperature decreases relative to the electron temperature.) Under these conditions the energy release in the electron gas is increased comparatively, since the recombination energy is now transferred to only a small number of electrons. As a result the drop in electron temperature takes place more slowly, and the recombination is also retarded. Under these new heat transfer conditions the degree of ionization ceases to approach zero and a residual ionization is retained in the gas (freezing takes place). However, unlike the preceding case, the residual ionization is now very low, since before the time the energy exchange between the electrons and ions is disturbed an appreciable number of the free electrons succeed in recombining.

Figure 8.13 presents curves of $x(t)$ calculated in [28] for two typical cases.

![Figure 8.13. Change in degree of ionization with time for expansion of a gas into vacuum (for explanation see text).](image)
of the sudden expansion of a gas cloud. In the calculations the ionization potential for the atoms was taken to be 13.5 ev and their atomic weight taken to be 14. Curve 1 pertains to the case when the degree of ionization at the time when the ionization equilibrium is disturbed is $x_1 = 0.58$ and the gas temperature and density are $T_1 = 12,000^\circ$K and $N_1 = 1.7 \cdot 10^{16}$ cm$^{-3}$, respectively. The time when the equilibrium is disturbed is $t_1 = 2 \cdot 10^{-6}$ sec. The radius of the gas cloud at this time is $R_1 = 4.9$ cm, and the expansion velocity $u = 24$ km/sec. The same flow variables given for the time when equilibrium is disturbed can be obtained with different initial conditions. In particular these results can correspond, for example, to an initial temperature, density, and cloud radius $T_0 = 50,000^\circ$K, $N_0 = 2 \cdot 10^{18}$ cm$^{-3}$, and $R_0 = 1$ cm, respectively. As can be seen from the figure, for these conditions the degree of ionization of the gas tends to the rather appreciable constant value of $\approx 0.2x_1 \approx 0.12$, and appreciable freezing takes place. Curve 2 relates to the following values of the parameters at the time when the equilibrium is disturbed: $t_1 = 2.1 \cdot 10^{-6}$ sec, $T_1 = 11,700^\circ$K, $N_1 = 4 \cdot 10^{16}$ cm$^{-3}$, $x_1 = 0.34$, $R_1 = 5$ cm, $u = 24$ km/sec. This case can correspond, for example, to the initial conditions: $T_0 = 50,000^\circ$K, $N_0 = 5 \cdot 10^{18}$ cm$^{-3}$, and $R_0 = 1$ cm. As can be seen, in this case the degree of ionization tends to zero, and it appears that no freezing takes place. Actually, as was noted above, the recombination will also cease at some stage (when the energy transfer from the electrons to the heavy particles slows down), but only when the degree of ionization is very low.

In concluding this section we wish to emphasize again that the diffusion of resonance radiation, which has not been taken into account here, aids in increasing the heat release in the gas, in decreasing the rate of recombination, and in increasing the residual ionization. This process should be considered in relation to the specific problem at hand, since the diffusion of resonance radiation depends on the dimensions and degree of transparency of the gas cloud, the character of the broadening of the spectral lines, the gas composition, etc.

4. Vapor condensation in an isentropic expansion

§10. Saturated vapor and the origin of condensation centers

If the vapor of any substance is isentropically expanded and cooled, there is some time $t$ at which the vapor becomes saturated; then it becomes super-saturated, after which condensation begins. It is well known that condensation is greatly facilitated by the presence of ions, dust, and other foreign particles which become condensation centers, about which liquid drops form.
Ions and dust particles only create favorable conditions for the more rapid formation of condensation centers, but their presence is not at all necessary. In a pure supersaturated vapor condensation centers appear as the result of the agglomeration of molecules into molecular complexes. After reaching the so-called critical size the complexes become stable and do not break up, and exhibit a tendency for further growth and transformation into droplets of liquid.

The phenomenon of vapor condensation in an isentropic expansion is met in industry, in the laboratory, and in nature. It serves as the basis of operation of the Wilson cloud chamber, which is widely used in nuclear physics for recording the motion of high-speed charged particles. The Wilson cloud chamber consists of a vessel filled with vapor of water, alcohol, or other liquid. The required supersaturation is created by an isentropic expansion of the vapor by means of a rapidly receding piston. The vapor condenses on the ions which are formed along the trajectory of the rapidly moving particle, and the drops of liquid are recorded by optical means. The condensation of the water vapor in air is frequently observed in the expansion of air in wind tunnels.

The fact that condensation must start at some time during an isentropic expansion of vapor can be easily explained with the aid of a temperature-specific volume diagram. As is known from thermodynamics, the pressure of a saturated vapor which is in equilibrium with the liquid is governed by the Clapeyron–Clausius equation (see, for example, [18]). If the vapor is considered as a perfect gas, then this equation leads to the following relationship between the specific volume of the saturated vapor $V_{vap}$ and the temperature*

$$V_{vap} = BT e^{U/RT}, \quad T = \frac{U}{R} \left( \frac{\ln V_{vap}}{BT} \right)^{-1}, \quad (8.38)$$

where $U$ is the heat of vaporization, $R$ is the gas constant, and $B$ is a coefficient, which can be taken approximately constant. It is evident from this equation that the saturation temperature has only a weak logarithmic dependence on the vapor volume. On the other hand, the isentrope for the vapor is a power-law type curve of the form $T \sim V^{-\gamma}$, which must intersect the saturation curve (Fig. 8.14). At the point of intersection $O$ the previously unsaturated expanding vapor becomes saturated.

Let us follow the process in time. If the vapor expands continuously, then the specific volume increases monotonically with time. Instead of considering the temperature change with time $T(t)$, we can consider the temperature

* This follows from the relations $p = const e^{-U/RT}$, $pV = RT$, where $p$ is the saturated vapor pressure. Editors' note. $U$ is assumed constant, and the specific volume of the liquid is assumed negligible.
§10. Saturated vapor and the origin of condensation centers

change with increasing volume \( T(V) = T[V(t)] \), using a \( T, V \) diagram (see Fig. 8.14). After passing the saturation state, the vapor continues to expand following the vapor isentrope, and becomes supersaturated (supercooled). The rate of formation of condensation centers has an extremely strong dependence on the degree of supersaturation. Therefore a further increase in

![Fig. 8.14. \( T,V \) diagram for condensation in an isentropic vapor expansion. I is the isentrope for the vapor, SV is the saturated vapor curve, O is the saturation point, TI is the isentrope for the equilibrium two-phase vapor-liquid system, Act is the actual curve for the vapor-liquid drop systems taking into account the kinetics of condensation.](image)

the degree of saturation results in a rapid increase in the number of nuclei in the liquid phase. Soon after the saturation state is passed, the rate of condensation reaches a value such that the release of the latent heat prevents any further increase in the supersaturation (if, of course, the expansion is not too rapid). The condensation accelerates even if the number of centers remains constant, because of an increase in the surface area of the drops to which the vapor molecules attach. The acceleration of the condensation not only stops the increase in supersaturation, but even leads to a decrease in the degree of supersaturation. The formation of new nuclei, which is highly sensitive to the value of supersaturation, ceases immediately and further condensation proceeds by means of the attachment of molecules to the previously formed drops. Thus all condensation centers, as a rule, are born at the very beginning of the condensation process, as soon as a sufficiently high degree of supersaturation is reached.

In the Wilson cloud chamber the vapor is rapidly expanded to a definite volume, so that a known initial supersaturation is established in the vapor. This supersaturation is chosen to be large enough that all the ions become condensation centers, thus making it possible to determine the number of ions by counting the number of drops*. Therefore, no problem arises as to the number of condensation centers.

It is another matter in gasdynamic processes such as the expansion of gases in wind tunnels, the exhaust from nozzles, or the sudden expansion of a gas cloud which forms as a result of the heating and vaporization of an

* At the same time, practically speaking, nuclei not containing ions do not form.
initially solid substance such as a metal. Here the rate of expansion is deter-
mined by the general dynamics of the process, and the number of condensa-
tion centers is unknown and depends on the expansion rate. Even if ions are
present in the gas (which, of course, does not always happen) by far not all
of them become condensation centers if the expansion rate is sufficiently low.
As a result of the factors already mentioned, the supersaturation of a system
can decrease due to very rapid condensation after only a few of the ions are
converted into condensation centers. Even more unknown is the number of
pure vapor centers in the absence of foreign particles. The number of conden-
sation centers depends on the maximum attainable supersaturation (super-
cooling) and is determined by the interplay of opposing effects: cooling of
the vapor corresponding to the work of expansion and heating of it as a
result of the release of latent heat in condensation. We shall show in §12
how one may calculate the number of condensation centers, knowing the
rate of expansion and cooling of the vapor.

§11. The thermodynamics and kinetics of the condensation process

Let us consider the process of condensation in an isentropically expanding
fluid from a purely thermodynamic point of view, by assuming that thermo-
dynamic equilibrium exists at any given time. Up to the time of saturation
the gas expands along an isentrope. After the saturation state has been reached
and condensation begins, the fluid becomes a two-phase vapor-liquid system.
The adiabatic equation is complicated because of the conversion of a part of
the gas phase into a liquid of different thermodynamic properties and because
of the release of the latent heat. The isentrope for this two-phase system
satisfies the adiabatic equation

\[
[c_1(1 - x) + c_2 x] \frac{dT}{V} + RT(1 - x) \frac{dV}{V} - [U - (c_2 - c_1)T] \, dx = 0. \tag{8.39}
\]

Here \(c_1\) is the specific heat of the vapor at constant volume; \(c_2\) is the specific
heat of the liquid; \(x\) is the degree of condensation, defined as the ratio of the
number of molecules in the liquid phase to the total number of molecules in
the given mass of fluid; \(V\) is the specific volume of the fluid, which is less by
a factor of \((1 - x)\) than the specific volume of the vapor: \(V = V_{vap}(1 - x)\)*.
In this equation we have neglected the surface energy of the liquid drops,
which is very small in comparison with the latent heat if the drops contain

* The specific volume of the two phase system is \(V = V_{lq}x + V_{vap}(1 - x)\), where \(V_{lq}\) is
the specific volume of the liquid phase. Since the density of the liquid is much higher than
the density of the vapor, for a degree of condensation which is not too close to unity, the first
term can be neglected and \(V \approx V_{vap}(1 - x)\). The specific heats of the liquid and the vapor
\(c_2 \) and \(c_1 \) in (8.39) are assumed to be constant.
large numbers of molecules. The adiabatic equation (8.39) is also valid in the absence of thermodynamic equilibrium. In the case of nonequilibrium, the degree of condensation \( x \) is determined by the condensation kinetics. Under conditions of thermodynamic equilibrium, for an infinitely slow expansion, the vapor is in equilibrium with the liquid at any instant of time, and is always saturated. The state of the fluid changes in this case along the saturation curve (8.38), which, if we replace the specific volume of the vapor by the specific volume of the fluid, takes the form

\[
\frac{V}{1 - x} = B T e^{U/RT}.
\] (8.40)

If we eliminate the degree of condensation \( x \) from (8.39) and (8.40), we obtain a differential equation describing the isentropic process in the two-phase system in terms of the variables \( T \) and \( V \). The solution of this equation yields the isentrope \( T(V) \). The constant of integration in the general solution is determined by the entropy of the fluid. The constant can be expressed in terms of the temperature and volume at the saturation point \( O \), since it is obvious that the isentrope passes through this point. We shall not write out the solution here, but shall instead illustrate the isentrope in Fig. 8.14. The solution lies somewhat below the saturation curve, which can be seen by comparing (8.38) and (8.40) and taking into account the fact that \( x > 0 \), \( 1 - x < 1 \). For a small degree of condensation, when \( x \ll 1 \), the isentrope of the two-phase system almost coincides with the saturation curve. The divergence of the two curves determines the degree of condensation \( x \):

\[
1 - x = \frac{V(T)}{V_{\text{vap}}(T)}.
\]

The degree of condensation increases monotonically along the isentrope with increasing volume.

It is interesting to note that in an infinite isentropic expansion of a fluid, with \( V \to \infty \) (and cooling to zero temperature \( T \to 0 \)), the degree of condensation along the isentrope for thermodynamic equilibrium tends to unity, \( x \to 1 \). In other words, according to the laws of thermodynamics, in the unlimited expansion of a fluid, the vapor should be completely condensed. In an isentropic expansion to a finite volume only a finite amount of vapor is condensed. In reality, of course, the state of the fluid in the condensation process can never follow the equilibrium isentrope exactly, it only more or less approaches the equilibrium state; it is closer to equilibrium, the slower is the change of the external conditions, i.e., the slower is the expansion.

It was already noted above that condensation centers are born primarily
immediately after passing the saturation state, at the time when maximum supersaturation is reached. Thereafter, if the expansion does not proceed too rapidly, the accelerating condensation stops the supersaturation process and no new nuclei are formed. The state of the fluid after passing through a point of maximum deviation from the equilibrium isentrope (TI) (Fig. 8.14, maximum supercooling) approaches the equilibrium state. The degree of supercooling, however, does not drop to zero and the curve (Act) never reaches the thermodynamic equilibrium curve (TI), always passing below the latter. Condensation now proceeds by the size of the droplets increasing. Two processes take place simultaneously: the forward process, attachment of vapor molecules to the drops, and the reverse process, evaporation of the drops. The rate of growth of the drops (that is, the condensation rate) is determined by the difference between the rates of the forward and reverse processes and is higher, the higher the degree of supersaturation. In the saturated vapor, for a state on the equilibrium isentrope, the adhesion and evaporation rates are exactly equal and the drops do not increase in size.

In condensation the degree of supersaturation adjusts to the balance between attachment and evaporation, automatically conforming to the process in such a manner that the attachment exceeds the evaporation and that the condensation rate follows the expansion of the fluid. The system is always in a state close to equilibrium, i.e., close to saturation.

An appreciable departure from thermodynamic equilibrium can take place only in a very strong expansion, when the attachments of vapor molecules become exceedingly rare. Thus, in the sudden expansion of vapor into vacuum the attachment rate, which is proportional to the vapor density and thus to $r^{-3}$, starting at a certain time is no longer capable of following the expansion; condensation ceases and the remaining vapor expands to infinity, again following the gas isentrope (Fig. 8.14). Freezing takes place, and the fluid expanding to infinity is not completely condensed, as would be required by the equilibrium laws of thermodynamics, but is partially in the form of a gas and partially in the form of condensate drops (for more details, see the following section). For a rapid expansion of a fluid, the condensation cannot “follow” the expansion and the state departs substantially from thermodynamic equilibrium from the very beginning. In a very rapid expansion to a given volume, as takes place in the Wilson cloud chamber, condensation does not take place during the expansion and begins only after the expansion has ceased. For a very rapid expansion into vacuum condensation generally does not occur at all and the fluid flows out to infinity in the gas phase. This corresponds to the maximum departure from thermodynamic equilibrium and to maximum freezing.

* The thermodynamic equilibrium isentrope, strictly speaking, corresponds to a saturated state with respect to a plane surface of the liquid, with respect to drops of infinite radius.
§12. Condensation in a cloud of evaporated fluid suddenly expanding into vacuum

In this section we consider in more detail the condensation process in the expansion of a vapor, setting out the basic scheme for quantitative calculations and presenting some numerical results. We shall examine condensation as it occurs in a cloud of evaporated fluid expanding into vacuum. Here, we have in mind the phenomenon of the explosion of large meteorites on impact with planet surfaces (devoid of atmosphere) or asteroid collisions, which were mentioned at the beginning of §6. We are interested in what the form is of the vaporized material of the planet soil and of the meteorite which expands into interplanetary space: Is the material in the form of a pure gas or in the form of minute particles, and if the latter what are the particle dimensions? A solution to this problem was obtained by one of the present authors [19].

All the numerical results will pertain to the condensation of iron vapor as applied to the case of vaporization of iron meteorites. Let us consider when saturation is reached in the expansion of iron vapor. In Table 8.1 we give the calculated vapor temperature $T_1$ and atom number density $n_1$ at the time of saturation for several values of vapor entropy $S$. Assuming that the expansion is isentropic, we can say that the "solid" iron at the time of heating had the same entropy $S$. The table gives the values of the initial energy of heating $e_0$ and temperature $T_0$ of standard density solid iron, corresponding to these values of the entropy. These quantities were calculated by the method described in §14, Chapter III (both the nuclear and the electronic contributions to the specific heat are taken into account). The last column gives the average velocities of sudden expansion of a gas sphere of iron atoms estimated from the equation $u = (2e_0)^{1/2}$ (see §6), that is, by assuming that the vapor is already strongly cooled before the time of condensation and that all the

<table>
<thead>
<tr>
<th>$e_0$, ev/atom</th>
<th>$T_0$, ev</th>
<th>$S_1$, cal/mole·deg</th>
<th>$T_1$, °K</th>
<th>$n_1$, cm$^{-3}$</th>
<th>$u$, km/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.6</td>
<td>5</td>
<td>48.3</td>
<td>3100</td>
<td>8.01 · 10$^{19}$</td>
<td>9.2</td>
</tr>
<tr>
<td>71.9</td>
<td>10</td>
<td>60.8</td>
<td>2130</td>
<td>7.15 · 10$^{16}$</td>
<td>15.5</td>
</tr>
<tr>
<td>138</td>
<td>15</td>
<td>71.5</td>
<td>1700</td>
<td>2.86 · 10$^{14}$</td>
<td>21.4</td>
</tr>
<tr>
<td>222</td>
<td>20</td>
<td>81.3</td>
<td>1430</td>
<td>1.43 · 10$^{12}$</td>
<td>27.2</td>
</tr>
</tbody>
</table>

* Some qualitative remarks on the phenomenon of condensation of vaporized matter were made by the present authors in [20].
initial heating energy has been converted into kinetic energy of the expansion.

Let us now estimate the number of condensation centers, that is, the num­
ber of condensate particles in the final state. The theory of the formation of
nuclei of the liquid phase in pure supersaturated vapor has been developed by
a number of authors, M. Volmer, R. Becker and W. Döring, L. Farkas, and
Zel'dovich and Frenkel. A detailed presentation of the theory with references
to original works may be found in the book by Frenkel [21] (see also [22]).
We shall recount here only main the ideas of the theory.

In the vapor phase there occur from time to time fluctuations during which
the vapor molecules join together forming molecular complexes, nuclei of
the liquid phase. In unsaturated vapor, when the gas phase is stable, the
complexes are unstable and soon break up (evaporate). In supersaturated
vapor only complexes of very small dimensions are unstable. The increase in
size of the smallest complexes by the attachment of new molecules is ener­
getically unfavorable, because of the increase in surface energy at the inter­
face between the liquid and the gas phases. On the other hand, the increase
in size of sufficiently large complexes is energetically favorable, since the
favorable volume energy effect (release of latent heat) becomes greater than
the unfavorable surface effect with sufficiently large dimensions. For each
degree of supersaturation there is a definite critical complex dimension.
Supercritical nuclei (with a radius larger than critical) are stable or “viable”,
and exhibit a tendency for further growth and transformation into liquid
droplets. The rate of formation of these viable nuclei of condensation centers
is proportional to the probability of appearance of critical size complexes.
The formation of these complexes requires the expenditure of a certain
energy $\Delta \Phi_{\text{max}}$ necessary to overcome the potential barrier, and hence,
according to the Boltzmann relation, the probability of such fluctuations is
proportional to $\exp(-\Delta \Phi_{\text{max}}/kT)$. The potential barrier $\Delta \Phi_{\text{max}}$ or activation
energy depends on the critical radius of the complex and is uniquely related
to the degree of supersaturation. This degree can be characterized, for exam­
ple, by the supercooling

$$\theta = \frac{T_{\text{sat}} - T}{T_{\text{sat}}}.$$  

Here $T_{\text{sat}}$ is the temperature of saturated vapor at the given density and $T$ is
the actual vapor temperature.

The rate of formation of viable nuclei, that is, the number of condensa­
tion centers per single vapor molecule which appear per unit time under
steady-state conditions, assuming that constant supersaturation (super­
cooling) is maintained in the system and the supercritical nuclei are removed
from the system as formed and replaced by an equivalent amount of vapor, is

\[ I = Ce^{-b/\theta^2}, \]  

(8.41)

where

\[ C = n\bar{v}2\omega\left(\frac{\sigma}{kT}\right)^{1/2}, \]

\[ b = \frac{16\pi\sigma^3\omega^2}{3k^3q^2T}. \]

Here \( n \) is the number of vapor molecules per unit volume, \( \bar{v} \) their thermal speed, \( \sigma \) the surface tension, \( \omega \) the volume of liquid per molecule, and \( q = U/R \) is the heat of vaporization expressed in degrees. The critical nucleus radius \( r^* \) is related to the degree of supersaturation by

\[ \theta = \frac{2\sigma\omega}{kqr^*}. \]

The theory can also be generalized to the case of electrically charged nuclei containing an ion (see [19]). The rate of formation of nuclei is again given by (8.41), except that the constant \( b \) is now smaller.

Let us set up the rate equation for condensation. We make the basic assumption that the expansion of the vapor proceeds sufficiently slowly that the process of formation of nuclei can be considered as quasi-steady. In this case, the rate of formation always coincides with the steady-state rate (8.41) corresponding to the actual supercooling \( \theta \) of the system at the given time. If \( I(t') \) is the number of condensation centers formed per unit time at the time \( t' \) (per vapor molecule), and \( g(t, t') \) is the number of molecules at the time \( t \) in a liquid drop born from a nucleus which appeared at the time \( t' \), then the degree of condensation at the time \( t \), \( x(t) \), can be written as

\[ x(t) = \int_{t_1}^{t} I(t')g(t, t') \, dt'. \]

(8.42)

The integration with respect to time is carried out from the time of saturation, that is, from the time when the nuclei begin to appear.

The rate of increase of a drop of supercritical size is equal to the difference between the rate of attachment of vapor molecules to the drop surface and the rate of evaporation from the drop. It can be written approximately as (see [19, 21])

\[ \frac{dg}{dt} = 4\pi r^2 n\bar{v}(1 - e^{-q/\theta^2}), \]

(8.43)
where $4\pi r^2$ is the surface area of the drop and $\nu$ is the flux of vapor molecules. The factor in parentheses is proportional to the difference between the attachment and evaporation rates. In the state of saturation, when $\theta = 0$, attachment and evaporation cancel each other and the rate of growth is equal to zero*. In supersaturated vapor $\theta > 0$ and the size of a drop increases on the average, with $dg/dt > 0$; in unsaturated vapor $\theta < 0$ and, on the average, the drop is evaporated, with $dg/dt < 0$.

Equations (8.42), (8.43), and (8.41), together with the adiabatic equation for a two-phase system (8.39), the formula for a saturated vapor (8.38), and the relation for the expansion of the fluid, which in the case of sudden expansion into vacuum is given by (8.25), form a complete system of equations for calculating the condensation kinetics.

In accordance with the qualitative picture presented in the preceding sections, we can break up the solution of this system into two independent stages. The first stage is the analysis of a small time interval immediately after the saturated state has been reached, during which the supercooling first increases, passes through a maximum, and then decreases because of the onset of condensation. The nuclei appear during this short stage. Calculating the number of the nuclei

$$n = \int_{t_0}^{\infty} I(t') \, dt',$$

we get the total number of condensate particles (per initial molecule). Actually, the integration with respect to time extends here not to $t = \infty$, but is carried over a rather small time interval, since by virtue of (8.41), the rate $I$ drops very sharply as soon as the supercooling, having passed through the maximum, begins to decrease. The second stage is the analysis of growth of the already known number of drops during all the ensuing states, up to $t \to \infty$.

A rigorous solution of the system of equations is, of course, very difficult. An approximate solution has been given in [19]. The approximate analysis of the first stage is based on the nature of the extremely sharp dependence $I(\theta)$, by virtue of which we can assume that practically all nuclei are formed in a very short time interval close to the time at which the supercooling is maximum (the solution actually gives an extremum for $\theta(t)$).

Referring for details of the solution to [19], we present here the results of calculations of a specific example. We consider a sphere of iron atoms with a mass of 33,000 tons, which is heated and converted into a dense gas, say, as the result of the impact of a very large iron meteorite on the surface of the moon. Let the impact velocity be such that the initial heating of the iron at standard density is $\varepsilon_0 = 72 \text{ ev/atom}$. The initial temperature in this case is

* The effect of the curvature of the drop is neglected here.
§13. Cosmic dust. Laboratory studies of condensation

$T_0 = 10 \text{ ev} = 116,000^\circ\text{K}$. In the stage of strong cooling at the time of vapor saturation the expansion is taking place practically by inertia, with an average velocity of $u = 15.5 \text{ km/sec}$. The vapor becomes saturated at $t_1 = 6.8 \cdot 10^{-2} \text{ sec}$ from the start of the expansion, with the corresponding radius of the cloud equal to 1050 m. In this case $T_1 = 2130^\circ\text{K}$ and $n_1 = 7.15 \cdot 10^{16} \text{ cm}^{-3}$.

For the sudden expansion of an initially highly ionized gas into vacuum, even in the stage of strong cooling some residual ionization is retained which is far above the value for thermodynamic equilibrium. The condensation centers in this case will contain ions. As shown by calculations, the number of condensation centers depends very weakly on whether or not they are charged, since the assumption that the condensation takes place on ions does not appear to be important.

The maximum possible supercooling in our example is found to be $\theta_{\text{max}} = 0.0765$ ($b/\theta_{\text{max}} = 43.1$). A nucleus of critical size for this supercooling contains 46 atoms. The number of condensation centers is $v = 4 \cdot 10^{-11}$ per atom, which is much smaller than the number of ions per atom, in contrast to the process in the Wilson cloud chamber, where all the ions become condensation centers.

Analysis of the second stage, during which the size of the drops increases, shows that during a long period of time the condensation follows the expansion of the fluid and a state close to equilibrium is maintained in the system. Only at the time $t_2 \sim 2.5 \text{ sec}$, when the sphere has expanded to 40 km, does the density of the fluid become so small that further growth of drops ceases and freezing begins. Up to this time (and thus over the entire process) approximately one half of the iron vapor is condensed. Knowing the degree of condensation $x_\omega$, and the number of condensate particles, we can also find their size (the number of atoms per particle is equal to $x_\omega v^{-1}$). In our example the iron particles suddenly expanding to infinity have a radius of $3.1 \cdot 10^{-5} \text{ cm}$; their total number is $3 \cdot 10^{21}$. Approximately half of the fluid goes out to infinity in gaseous form.

We can establish theoretically approximate similarity relations for transforming to other initial conditions. It appears that for sufficiently slow expansions, when the initial assumptions are valid, the degree of condensation of the given fluid for a sudden expansion to infinity is independent of the initial conditions, and that the size of the condensate particles is proportional to the initial linear dimensions of the vaporizing body (to the cube root of the mass), and decreases rapidly with an increase in initial heating.

§13. On the problem of the mechanism of formation of cosmic dust. Remarks on laboratory investigations of condensation

There are some reasons to believe that the process of condensation of a vaporized substance suddenly expanding into vacuum, which was considered
in the preceding section, is one of the mechanisms of formation of cosmic dust in the solar system (this hypothesis was proposed in [19]). Interplanetary space contains small particles of various sizes, which are called cosmic dust. Sometimes these particles fall on the earth in the form of meteor showers. In their motion about the sun the particles experience some slowing down from the aberration component of the light pressure (Poynting–Robertson effect, eds.)*. The very small particles with sizes of the order of $10^{-6}$–$10^{-5}$ cm fall into the sun and disappear (for further details see [23]). Consequently, the solar system must have a source for replenishing the store of these very small particles of cosmic dust. It was noted (in particular by Stanyukovich), that this source may be the mechanical disintegration of matter in the collisions of small bodies of the solar system (asteroids), or in meteorite impacts on the surfaces of planets devoid of atmosphere. The particles produced have acquired considerable velocity, overcome the gravity field, and, not being slowed down by an atmosphere, fly out into space.

It is reasonable to assume that the phenomenon we have discussed of condensation of vaporized matter of planet soil, meteorites, or asteroids is also a source of these very small particles. In energetic collisions of asteroids, when the kinetic energy of impact is sufficient for complete vaporization of both colliding bodies, mechanical disintegration of the solid is, in general, not present, since the entire mass is completely vaporized. In this case the condensation mechanism is the only one capable of forming the small particles. The liquid droplets, which have grown in the process of condensation, gradually cool down and solidify due to the energy losses from thermal radiation. It can be shown that the process of radiation cooling proceeds much more quickly than the evaporation of the heated particles, which slows down very rapidly as the vapor is cooled. Thus, the condensate particles which were already created will continue to exist in the form of solid dust particles. Since bodies colliding in space have very different sizes and velocities, the condensate particles which are formed are also of various sizes.

The phenomenon of the condensation of a vaporized substance in a gas-dynamic expansion can be also used for laboratory investigation of the condensation of vapors of metals and other solids (and liquids) and for the study of optical properties of very small particles. The dimensions of the condensate particles depend on the initial conditions; hence by properly choosing these conditions it is possible to obtain particles of the desired size.

* The light pressure acts basically in the radial direction. The force due to this pressure is inversely proportional to the square of the distance between the particle and the sun, and its effect is equivalent to only a small decrease in the gravitational force; the radial component of the light pressure affects only the radius of the orbit. The slowing down, however, is due to the component of the light pressure which is tangent to the orbit and which arises from the aberration of light. For additional details see the book by Fesenko [23].
in the laboratory. We present here the results of some rough estimates for conditions close to those encountered in the laboratory. If we rapidly vaporize 1 g of iron by transferring to it in some manner an initial energy of $\epsilon_0 = 13$ ev/atom, corresponding to the initial temperature (at the density of the solid metal) of $T_0 = 35,000^\circ$K, then the condensation of the vapor in a sudden expansion into vacuum (in an evacuated vessel) ends at the time $t = 5 \cdot 10^{-5}$ sec, when the cloud has expanded to 30 cm. The dimensions of the condensate particles in this case will be of the order of $10^{-4}$ cm.

The calculations of condensation kinetics can be easily carried over to other relationships governing the expansion of a fluid which takes place, say, in a wind tunnel or in a nozzle exhaust. These calculations do not involve anything basically new in comparison with the case of sudden expansion into vacuum, and we shall not consider them. We note that if the degree of condensation is not too high, or if the total energy of the vapor is much greater than the heat of vaporization, then the effect of the condensation on the gasdynamics of the process is very small. The kinetics of condensation can then be calculated on the basis of the known gasdynamic solution, found in first approximation without taking condensation into account. This is exactly the procedure which we followed in the preceding section.