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Mixing of real and quantum gases†

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Through the consistent application of quantum statistical thermodynamics, functions of isothermal mixing of real rarefied gases and quantum gases in states of varying degrees of degeneracy are obtained. The reasons for the emergence and resolution of the ''Gibbs paradox'' and other ''paradoxes'' are analyzed. Numerical calculations of entropy and pressure jumps were performed using the example of a pair of Bose gases (neon and argon) and a pair of Fermi gases (electron and muon). The derived thermodynamic relationships make it possible to determine other effects under mixing conditions other than isothermal – changes in entropy, temperature, pressure, energy, and thermal effect.

1. Introduction

It would seem that the thermodynamics of mixing of quantum gases is of abstract, purely theoretical interest. However, thanks to the success of laser methods of deep cooling,[1] the possibility of studying various effects in mixtures of degenerate Fermi and Bose gases has opened up. All kinds of statistical mixtures have been realized using different combinations of atomic species, Bose–Bose, Fermi–Fermi, and Fermi–Bose. Thus, the heteronuclear mixtures of quantum-degenerate gases were realized in 2001 with a Bose–Bose combination of ^{41}K and ^{87}Rb atoms.[2] In the same year a Fermi–Bose mixture of ^{6}Li and ^{7}Li was obtained.[3,4] Later, in 2008 the first quantum-degenerate two-species Fermi–Fermi mixtures were obtained with ^{6}Li–^{40}K.[5,6]

There are no specific examples in the literature using the thermodynamics of mixing of rarefied classical gases. In private communications with inorganic chemists involved in the synthesis of fullerene derivatives using the gas phase, such examples were encountered, as well as with industry representatives who developed a new type of reactor for the synthesis of urea.

Moreover, numerical calculations for quantum gases in significantly different degrees of degeneracy may be useful for studying the possibility of muon catalysis of thermonuclear fusion. Back in 1947, Frank, while studying the results of a cosmic ray experiment, suggested that mesons could catalyze fusion reactions.[7] This idea led to further theorizing on the subject[8–11] and attempts to calculate the design of specific reactors.[12]

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Upon closer examination, the thermodynamic effect of mixing of different and identical gases turns out to be trivial only for perfect (ideal) gases. The only work directly related to the content of the present paper is the work of Bazarov,[13] devoted to the explanation of three paradoxes (Gibbs, Einstein and the temperature paradox). The author showed that all three paradoxes have the same physical cause – a jump of the partial density of a gas during the transition from its mixing with an arbitrarily close gas to mixing with an identical gas. Taking this jump into account makes it possible to explain the paradoxes mentioned above. In this case, the author limited himself to considering only weakly degenerate Fermi and Bose gases.

In our paper we will analyze these and other issues from different points of view and in more detail. The mixing of not only perfect, but also rarefied real gases, as well as completely degenerate quantum gases and gases in states close to and far from degeneracy will be considered. The main attention is paid to changes in entropy and pressure during mixing. The results obtained make it possible to calculate changes in other properties – energy, enthalpy, temperature – for various methods of reversible mixing – isothermal, adiabatic, and isobaric, as well as to determine the thermal effect of these processes. In all cases, we do not use a smooth transition from different gases to identical ones, and we do not give explanations for ''paradoxes'', since with the consistent application of quantum statistics, paradoxes do not arise.

In order to avoid cluttering the formulas we will use the number of particles (N) for the amount of gas, and measure the temperature in energy units. Then entropy is a dimensionless quantity and is equal to the natural logarithm of the number of microstates: $S = \ln W$. The transition to practical units comes down to the following replacement in the formulas: T(K) → T(J)/k_B, S(J K^{-1}) → $k_B S$ (dimensionless), where k_B is Boltzmann's constant.

Let us first look at some important issues.

2. Perfect gas concept

First of all, let us define what we call a perfect gas. There is the following definition: a gas in which particle interactions can be neglected (definition A). The ideality condition is that the average particle interaction energy is small compared to the average kinetic energy. In ordinary (non-quantum) gases, this requires that the average distance between particles be much greater than the characteristic size of the particles themselves, *i.e.*, that the gas be extremely rarefied.

This definition has a drawback, since a closer look reveals its ambiguity. The fact is that interaction is understood as the force interaction of particles through the physical fields created by them. Meanwhile, at a gas density of identical particles that still allows the force interaction to be neglected, exchange interaction can already play a significant role, unrelated to the usual forces acting between particles, but leading to their effective interaction, depending on the spin of the particles. This phenomenon, associated with the identity (indistinguishability) of particles of the same kind, has a purely quantum nature. When applied to gas, it leads to the fact that even in the complete absence of force interaction, the behaviour of the gas has nothing in common with the usual properties of a perfect gas. In particular, the Clapeyron equation of state $PV = NT$ loses its validity.

Exchange effects manifest themselves at high densities and low temperatures, therefore quantum behaviour mainly applies to the electron gas in metals, which has a characteristic density of $\sim 10^{28}$ electrons per m^3, which is three orders of magnitude higher than the concentration of perfect gas molecules under normal conditions. Electron gas is the most important representative of quantum gases, consisting of fermions – particles with half-integer spin, and therefore subject to Fermi–Dirac statistics.

From the Clapeyron equation it follows that at a given temperature the pressure of a perfect gas increases in proportion to the particle concentration $P \sim N/V$ or density, and at absolute zero temperature the pressure is zero at any finite particle density. This means that at $T = 0$ such a gas has infinite compressibility. For comparison, the dependence of pressure on the electron gas concentration in a state of complete degeneracy, which is realized at $T = 0$, has the form $P = \text{const}\cdot(N/V)^{5/3}$. The Fermi gas acquires this state at temperatures much lower than the degeneracy temperature $T \ll T_{0F}$. The expression for T_{0F} is given in Table 1. In a completely degenerate Fermi gas, all states of translational motion of particles with energy below the level ε_F (Fermi level) are occupied, and higher states are not occupied at all.

The above dependence $P(N/V)$ shows that, unlike a perfect gas, its energy and pressure do not vanish even at $T = 0$, *i.e.* the gas resists decreasing in volume. In other words, the electron gas has finite compressibility even at absolute zero temperature. This behaviour is fundamentally different from a perfect gas. The reason is that, due to the Pauli's exclusion principle, each quantum state can be occupied by only one electron; only

Table 1 Definitions of some quantities, their designations and dimensions

Quantity	Formula	Dimension	Useful ratios
Quantum volume	$V_Q = \left(\frac{2\pi\hbar^2}{mT}\right)^{3/2}$	m^3	
Second virial coefficient	$B = \frac{1}{2}\int\left(1 - e^{-\frac{u_{12}}{T}}\right)dV$	m^3	$2B' + TB'' = 0$
van der Waals parameters	a	J m^3	$a = (b - B)T$
	b	m^3	$b = B + TB'$
Isobaric heat capacity	$C = \left(\frac{\partial U}{\partial T}\right)_V$	Dimensionless	
Heat of volume change	$l = \left(\frac{\partial U}{\partial V}\right)_T + P$	Pa	
Isobaric thermal expansion coefficient	$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$	K^{-1}	
Isothermal compressibility coefficient	$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$	Pa^{-1}	
Isochoric pressure coefficient	$\gamma = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V$	K^{-1}	
Fermi gas degeneracy temperature	$T_{0F} = \frac{1}{2}\sigma\left(\frac{N}{V}\right)^{2/3}$	K	
Bose gas degeneracy temperature	$T_{0B} = \frac{3.31}{g^{2/3}}\frac{\hbar^2}{m}\left(\frac{N}{V}\right)^{2/3}$	K	
Abbreviations	$\sigma = \left(\frac{6\pi^2}{g}\right)^{2/3}\frac{\hbar^2}{m}$	$J^2\ c^2\ kg^{-1}$	$\frac{\sigma_1}{\sigma_2} = \left(\frac{g_2}{g_1}\right)^{2/3}\frac{m_2}{m_1}$
	$\rho = \left(\frac{\pi g}{6}\right)^{2/3}\frac{m}{\hbar^2}$	$kg^{-1}\ J^{-2}\ c^{-2}$	$\frac{\rho_1}{\rho_2} = \left(\frac{g_1}{g_2}\right)^{2/3}\frac{m_1}{m_2}$
	$\kappa = \frac{1}{2g}\left(\frac{\pi\hbar^2}{m}\right)^{3/2}$	$J^{3/2}\ m^3$	$\frac{\kappa_1}{\kappa_2} = \frac{g_2}{g_1}\left(\frac{m_2}{m_1}\right)^{2/3}$

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two electrons are at the ground energy level of translational motion. The remaining electrons are located at levels with higher kinetic energy, and therefore, having momentum, exert pressure on the walls. This is one of the manifestations of the indistinguishability of particles in combination with other principles of quantum mechanics.

It should be particularly emphasized that the results described above for the electron gas are obtained without taking into account the Coulomb repulsion of electrons, so from this point of view the gas could be called perfect (in the sense of definition A). Moreover, as strange as it may seem at first glance, a degenerate electron gas becomes more perfect the higher its density.[14] This is due to the rapid increase in the Fermi level with increasing density $\varepsilon_F \sim (N/V)^{2/3}$. In this case, the average kinetic energy of electrons, which coincides in order of magnitude with the boundary energy ε_F, grows faster than the potential energy of the Coulomb interaction $u_{12} \sim (N/V)^{1/3}$, and therefore the ideality condition is better fulfilled with increasing N/V.

The exact opposite situation occurs if gas particles have integer spin (bosons) and therefore obey Bose–Einstein statistics, in which any number of particles can occupy the same quantum state. At a temperature below the degeneracy temperature of the Bose gas T_{0B} (see Table 1), the gas also becomes degenerate, but the essence of degeneracy is different: particles must accumulate in a state with the lowest energy ($\varepsilon = 0$). Number of particles with zero energy $N(\varepsilon = 0) = N[1 - (T/T_{0B})^{3/2}]$. At $T = 0$, all particles will fall into this state.

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Calculations show[14] that at $T < T_{0B}$ the pressure $P \sim T^{5/2}$ and does not depend at all on the volume. This circumstance is a natural consequence of the fact that particles in a state with zero energy do not have momentum and therefore do not make any contribution to the pressure.

If we define a perfect gas as a substance whose behaviour is subject to its specific equation of state $PV = NT$ (definition B), then the disadvantage of definition A disappears. Thus, the thermodynamic definition of a perfect gas assumes that the gas is sufficiently rarefied – so much so that not only the force interaction between particles can be neglected, but also quantum effects associated with the possibility or impossibility of two or more particles being in the same quantum state. In statistical thermodynamics, such a gas is said to be in the Boltzmann regime. This regime is realized when the average population of particle states (numbered by index k) is much less than unity ($\bar{n}_k \ll 1$), that is, the gas is sufficiently rarefied. In other words, the number of particle states (the vast majority of which for molecules are always states of translational motion) is much greater than the number of particles N in the gas. As a result, the absolute majority of states are vacant. This is the reason why the Pauli's exclusion principle (for fermions) becomes unimportant, as does the possibility of an arbitrarily large number of particles occupying the same state (for bosons). As a result, the quantum properties of the gas are practically not manifested. In what follows, a perfect gas will be understood as a gas according to definition B.

All thermodynamic properties of a one-component closed system are determined by a set of two equations – thermal (1) and caloric (2) equations of state. For a perfect gas they read:

$$P = NT/V, \tag{1}$$

$$U = U_0 + C_V T. \tag{2}$$

In eqn (2) U_0 is the conventional energy reference level, and C_V is the isochoric heat capacity. For a "true" perfect gas, that is, a gas consisting of particles without internal degrees of freedom, and therefore capable only of translational motion, $C_V = 3/2N =$ const. Then the energy of the gas depends linearly on temperature. This almost always occurs for monatomic gases. Although atoms have internal (electronic) degrees of freedom, they make virtually no contribution to the energy of the gas (and, accordingly, to its heat capacity), since excitation of electronic states usually requires energy measured in electron volts, and 1 eV corresponds to a temperature of 11 605 K. Note that as we approach such a high temperature, we can no longer talk simply about the population of excited electronic states: almost all atoms will already be ionized, and the gas will actually be a plasma.[14] For molecular gases, due to the rotational and vibrational degrees of freedom, C_V can significantly depend on temperature, but this will not affect the equation of state (1) in any way.

3. Mixing of perfect gases

It is useful to consider the mixing of perfect gases from different points of view. Let us start with the classical approach based on entropy using expression (S2) or (S10) (ESI†). The first of them was obtained purely thermodynamically, and contains a fundamentally unknown constant. The second is with the use of statistical thermodynamics, and gives absolute entropy within the limits of applicability of the quasi-classical approximation.

Let there be a thermally insulated vessel of constant volume V, separated by a solid fixed partition, on opposite sides of which there are two different gases in quantities N_1 and N_2 with the same temperatures and pressures, occupying volumes V_1 and V_2 (Fig. 1a). A vessel with gases is therefore an isolated system. Before mixing, the total entropy of gases was (i – initial)

$$S^{(i)} = N_1 \ln\frac{eV_1}{N_1} + N_2 \ln\frac{eV_2}{N_2} - N_1 f_1' - N_2 f_2'. \tag{3}$$

After mixing (as a result of removing the partition), each of the gases will occupy a volume $V = V_1 + V_2$, and the entropy of the mixture will become equal to (f – final)

$$S^{(f)} = N_1 \ln\frac{eV}{N_1} + N_2 \ln\frac{eV}{N_2} - N_1 f_1' - N_2 f'. \tag{4}$$

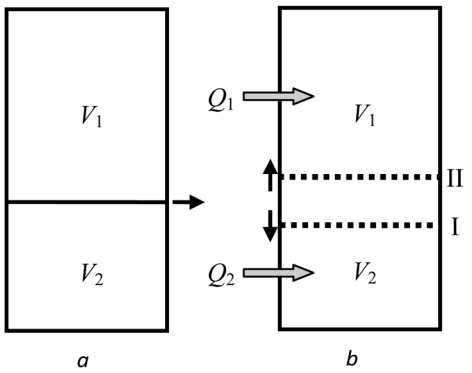

Fig. 1 Schemes of irreversible (a) and reversible (b) mixing of two gases.

Entropy change

$$\Delta S^{(\mathrm{id})} = S^{(\mathrm{f})} - S^{(\mathrm{i})} = N_1 \ln\frac{V}{V_1} + N_2 \ln\frac{V}{V_2}. \quad (5)$$

Since according to (1) at the same pressures and temperatures, the volumes of gases are proportional to the number of particles and $N_1 + N_2 = N$, then

$$\Delta S^{(\mathrm{id})} = N_1 \ln\frac{N}{N_1} + N_2 \ln\frac{N}{N_2}. \quad (6)$$

This quantity (entropy of mixing) is positive ($N > N_1, N_2$), as it should be due to the irreversibility of the process. If both gases were the same, then $f_1 = f_2 = f$, and after combining the vessels, the entropy would be equal

$$S^{(\mathrm{f})} = (N_1 + N_2)\ln\frac{V_1 + V_2}{N_1 + N_2} - (N_1 + N_2)f'. \quad (7)$$

But since, due to the equality of pressures and temperatures

$$\frac{V_1 + V_2}{N_1 + N_2} = \frac{V}{N} = \frac{V_1}{N_1} = \frac{V_2}{N_2} = \frac{T}{P},$$

we would have

$$\Delta S^{(\mathrm{id})} = N_1 \ln\frac{V}{N}\frac{N_1}{V_1} + N_2 \ln\frac{V}{N}\frac{N_2}{V_2} = 0, \quad (8)$$

that is, the entropy change would be zero. In our calculations, we took advantage of the fact that entropy is a function of state, and its change between two given states does not depend on the path of transition from one to another. Here we are dealing with an irreversible process, when in the initial and final states the gases are in equilibrium, and a spontaneous transition occurs through nonequilibrium states.

Is it possible to reversibly mix different gases? Let us again take a vessel with a fixed volume V, but now we must abandon its adiabatic isolation from the external environment in order to ensure isothermal expansion of gases for reversible mixing. In fact, when gases expand, they do work, and to maintain the temperature, heat must be supplied to them. Therefore, we will assume that the vessel is in thermal contact with a thermostat with a constant temperature T.

A reversible process must be quasi-static. For identical gases this can be done as follows. Let us imagine that the partition separating the various gases 1 and 2 consists of two semi-permeable partitions I and II, folded together (Fig. 1b). Partition I is permeable only to gas 1, and partition II is permeable only to gas 2. By moving partition I infinitely slowly, we will force gas 1 to expand from the initial volume V_1 to the final volume V. Now, in the same way, we will expand gas 2 by moving partition II. At both stages, gases perform work, expending their internal energy. If we want the mixing process to be isothermal, it is necessary to abandon the adiabatic insulation of the vessel with gases, then the energy of the gases, and therefore the temperature, will be maintained due to the absorption of heat $T\mathrm{d}S$ from the external environment. Based on (S1) (ESI†) taking into account $\mathrm{d}T = 0$, we have

$$\Delta S^{(\mathrm{id})} = N_1\int_{V_1}^{V}\frac{\mathrm{d}V}{V} + N_2\int_{V_2}^{V}\frac{\mathrm{d}V}{V} = N_1 \ln\frac{N}{N_1} + N_2 \ln\frac{N}{N_2}, \quad (9)$$

which coincides with (10) in accordance with the fact that the change in entropy as a function of state cannot depend on the method of transition between given states.

Formula (9), if applied to identical gases, leads to a paradoxical conclusion: the increase in entropy remains, while the final state of the system is macroscopically no different from the initial one, and entropy should not change. Otherwise, this would contradict one of the fundamental properties of entropy – additivity.

To resolve this paradox, it is enough to note that our reasoning is not applicable to identical gases. Indeed, it is obvious that a complex partition with combined partitions I and II does not allow either gas to pass through, so it is fundamentally impossible to mix identical gases in the manner described above.

Before the creation of quantum theory, in order to more clearly illustrate the Gibbs paradox, reasoning about the gradual transition from different particles to identical particles was practiced. An example would be the imaginary colouring of particles in different colours (for example, black and white), while in all other respects the particles are exactly the same. Then, mentally, ''bleaching'' is carried out (the gradual transformation of ''black'' particles into ''white''), ultimately leading to their complete identity. This transition (the moment when the particles become indistinguishable) must be accompanied by an abrupt decrease in entropy to compensate for its increase according to formula (9), thereby ensuring the expected and observed constancy of entropy. But according to the second law of thermodynamics, a spontaneous decrease in entropy in an adiabatically isolated vessel is impossible. Consequently, the erasing of differences between particles should occur as a result of an external influence on the system, reducing entropy. By the time the difference disappears, the entropy will decrease to the value of the entropy of a system with identical particles, which resolves the supposed ''paradox''.

Formula (9) is applicable only when the atoms or molecules are different, no matter how small the difference. Is it possible to assume that the properties of the atoms of one gas can gradually approach the properties of the atoms of another gas, ultimately making the atoms identical? From the point of view

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of classical mechanics, this is quite possible. For example, the sizes of atoms, determined by the sizes of classical electron trajectories (orbits), can be any, that is, they can be smoothly changed. In the classical description of natural phenomena, the explanation of the Gibbs paradox encounters significant difficulties. From the point of view of quantum theory, differences between particles, even between atoms of different isotopes of a certain chemical element, are of a much deeper nature, for example, due to differences in nuclear spins, not just nuclear masses. And generally speaking, the states of quantum systems are discrete. Thus, the sizes of atoms of different elements cannot be infinitely close to each other – they are determined by an abrupt change in the wave functions of the electron shells, even when replacing one isotope with another. Therefore, the passage to the limit described above is impossible.

Thus, the positive value of the entropy of mixing is due to the difference in the molecules of the gases being mixed. An increase in the entropy of a system is a criterion for the spontaneity of a process only if it is isolated or adiabatically isolated. This is inevitably linked with the need to expend work to separate one gas from another. The minimum work in this case is equal to ΔF – the increase in Helmholtz energy as a result of the separation of gases, since the total volume of the system and its temperature are constant. This is a special case when the criteria for the process to be spontaneous $(\Delta S)_{U,V} > 0$ и $(\Delta F)_{T,V} < 0$ coincide. In fact, during mixing the temperature and energy change are constant $\Delta U = 0$. This would be the case if the vessel was in a medium with a temperature equal to the temperature of the gases, since there is no exchange of heat with the medium. We have, therefore, $\Delta F = \Delta U - T\Delta S = -T\Delta S$, that is, the decrease in Helmholtz energy is proportional to the increase in entropy. This means that from the process of mixing two different gases under these conditions, it would be possible to extract a maximum work equal to $-\Delta F$. Conversely, using the same work, you can achieve separation of mixed gases.

Let us express once again in other words the essence of the Gibbs paradox. This arises due to the fact that formula (6) does not contain any characteristics of gases, for example, molar mass, and it supposedly should be valid for identical gases. It turns out that after removing the partition separating identical gases, entropy increases. But if the partition is reversibly restored, then it does not follow from anywhere that the entropy should decrease, and therefore one can think that the same equilibrium system has different entropies depending on the history of its formation.

Some believe that the existence of ΔS depends on the accuracy of determining the difference between the components being mixed, which is available with the available technology. That is, we can consider gases the same or different based on experiment. This looks strange, but is apparently being done in order to resolve the Gibbs paradox, remaining only within the framework of classical (not quantum) theory. There is really no need for this. After all, formula (7), thanks to which $\Delta S = 0$ is obtained, was used precisely because we previously consider the gases to be identical (indistinguishable). And on what basis? Here it is appropriate to turn to quantum concepts.

One of the key principles of quantum mechanics is the principle of indistinguishability of identical particles. It follows from it that the quantum state does not change with the rearrangement of any pair of particles, and therefore, with any rearrangements in general. Then $\Psi(\xi_1, \xi_2) = e^{i\alpha}\Psi(\xi_2, \xi_1)$. Symbol ξ denotes the arguments on which the wave function of the particle system depends. If we use the coordinate representation of the wave function, then $\xi = \{x, y, z, \sigma\}$, where σ is a spin variable that runs through $2s + 1$ values at the particle spin s. The fact is that in quantum mechanics, wave functions that differ only in the phase factor $e^{i\alpha}$ (the modulus of which is equal to unity) describe the same state. Repeated rearrangement of particles will again give a multiplication by $e^{i\alpha}$, *i.e.*, as a result, Ψ will be multiplied by $e^{2i\alpha} = 1$, since the wave function after two rearrangements should become the same. It follows that $e^{i\alpha} = \pm 1$, *i.e.*, when identical particles are rearranged, function Ψ either changes sign or does not change at all. This leads to the division of all particles in nature into two non-overlapping categories. It turns out that the sign of Ψ changes for particles with half-integer spin (fermions) and does not change for particles with integer spin (bosons).

From the above it follows that in quantum mechanics identical particles (for example, electrons) are not just identical, but fundamentally indistinguishable. Indeed, if at the initial moment, as a result of measuring coordinates, both particles were localized in non-overlapping regions of space (and they can be distinguished and numbered), then at subsequent moments their wave functions will "spread" in space (the so-called spreading of the wave packet) and will overlap. When measuring the coordinates of particles (their localization) again, it will no longer be possible to say which particle (with what number) was registered. If electrons had a trajectory, then their movement could be followed, and at any moment it would be possible to indicate where this or that electron is located.

Returning to the Gibbs paradox, we note that the use of formula (7) assumes precisely this indistinguishability. In the case of different gases, the indistinguishability of the particles of each of them would be taken into account by dividing by $N_1!N_2!$, and in the case of identical gases – by $(N_1 + N_2)! = N!$. The ratio of the second number to the first is a jump in the number of microstates of the system when different gases are replaced by identical ones, and the logarithm of the ratio is a jump in entropy during such a replacement. Using the Stirling formula for factorials $\ln N! \approx N\ln N - N$, we will have:

$$\Delta S = \ln\frac{N!}{N_1!N_2!} = N_1\ln\frac{N}{N_1} + N_2\ln\frac{N}{N_2}.$$

As can be seen, the increase in the total entropy of separated gases when replacing different gases with identical ones coincides with the result (6) or (9). After removal of the septum, no macroscopic processes occur, and no paradox arises.

Before finishing the consideration of perfect gases, we point out that Boltzmann and completely degenerate gases (two opposites) have states from which it is convenient to calculate thermodynamic functions. The state of a rarefied gas is close to perfect (designation: subscript B), and that of an almost degenerate gas is close to completely degenerate (designation: subscript 0). In Table S1 (ESI†), where expressions for the most important thermodynamic properties of gases are given, this is

reflected in the presence of the initial term, for example, P_B and P_0. Deviations are correction terms in the power series expansion. In the first case, the expansion occurs in the terms of the small parameter Nv_0/V (v_0 is the "volume" of the molecule), in the second – terms of the parameter $\exp[(\mu - \varepsilon)/T]$ (ε is the particle energy, μ is the chemical potential of the gas).

In addition, we introduce the notation $N_1/V_1 = x_1$, $N_2/V_2 = x_2$, $V_2/V_1 = A$, $1/(1 + A) = \lambda$, that we will use in the future in order to simplify the formulas. All the necessary relationships with these notations and notations themselves are given in Table S2 (ESI†). In numerical calculations it is assumed everywhere $A = 2$, respectively, $\lambda = 1/3$, and the total amount of gases is 1 mole. The parameters of two pairs of Fermi and Bose gases chosen for the calculations are given in Tables 2 and 3.

In the new notation, changes in pressure $(\Delta P)_{1,2} = P^{(f)} - P^{(i)}{}_{1,2}$ after mixing at arbitrary concentrations x_1 and x_2 are different:

$$P_1^{(i)} = Tx_1, \quad P_2^{(i)} = Tx_2, \quad P^{(f)} = T[\lambda x_1 + (1-\lambda)x_2],$$
$$(\Delta P)_1 = T(1-\lambda)(x_2 - x_1), \quad (\Delta P)_2 = -T\lambda(x_2 - x_1).$$

It follows that $\Delta P = 0$ only when $x_1 = x_2 = x$, and this does not depend on the ratio of the initial volumes (A). The entropy of mixing of two different perfect gases has the form

$$\Delta S_B = -N_1 \ln \lambda - N_2 \ln(1 - \lambda)$$

for any equal concentrations and any A. The symbol B indicates a gas in the Boltzmann regime, that is, a perfect gas.

If the gases are identical ($V_{Q1} = V_{Q2} = V_Q$, $g_1 = g_2 = g$), then according to (6)

$$S_B^{(i)} = N_1\left(-\ln\frac{xV_Q}{g} + \frac{5}{2}\right) + N_2\left(-\ln\frac{xV_Q}{g} + \frac{5}{2}\right),$$
$$S_B^{(f)} = (N_1 + N_2)\ln\frac{xV_Q}{g} + \frac{5}{2}(N_1 + N_2).$$

Subtraction of these expressions leads to the result $\Delta S_B = 0$.

4. Mixing of rarefied real gases

In this section, by rarefied gas we mean a gas with a virial equation of state with only the second virial coefficient B retained:

$$P = \frac{NT}{V}\left(1 + \frac{N}{V}B\right) = T(1 + Bx)x. \qquad (10)$$

As is known, B is a function only of temperature, in statistical thermodynamics it is a form of taking into account pair interactions between molecules, and is expressed by the following integral over the volume of gas:

$$B(T) = \frac{1}{2}\int\left(1 - e^{-\frac{U_{12}}{T}}\right)dV.$$

In this formula, $U_{12}(r)$ is the potential energy of interaction between two particles as a function of the distance between them. Note that B can take both positive and negative values, depending on the ratio of attractive and repulsive forces

Table 2 Numerical values of the most important parameters of two Fermi gases

Gas	Mass	Spin	Statistical weight	Volume concentration	Degeneracy temperature	Quantum volume	Multipliers in expressions for quantum gases containing fundamental constants		
	m, kg	s	g	N/V, m^{-3}	T_{0F}, K	V_Q, m^3	σ, J^2 s^2 kg^{-1}	ρ, kg J^{-2} s^{-2}	κ, J$^{3/2}$ m^3
Electronic	9.11×10^{-31}	1/2	2	1.00000×10^{27}	4234	7.98×10^{-26}	1.17×10^{-37}	8.44×10^{37}	1.88×10^{-57}
				9.42828×10^{25}	877				
Muonic	1.88×10^{-28}	1/2	2	1.00000×10^{27}	20.5	2.68×10^{-29}	5.66×10^{-40}	1.75×10^{40}	6.32×10^{-61}
				1.63243×10^{26}					

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Table 3 Numerical values of the most important parameters of two Bose gases

Gas	Mass	Spin	Statistical weight	Volume concentration	Degeneracy temperature	Second virial coefficient	van der Waals parameters	Quantum volume	
	m, kg	s	g	N/V, m^{-3}	T_{0B}, K	B, m^3	a, J m^3	b, m^3	V_Q, m^3
Neon ($_{10}Ne^{20}$)	3.32×10^{-26}	0	1	10^{30}	8.03	1.42×10^{-29}	5.89×10^{-50}	2.84×10^{-29}	1.15×10^{-32}
				10^{25}	0.0037				
Argon ($_{18}Ar^{40}$)	6.64×10^{-26}	0	1	10^{30}	4.02	-3.725×10^{-29}	3.76×10^{-49}	5.35×10^{-29}	4.05×10^{-33}
				10^{25}	0.0019				

between the molecules. The applicability of eqn (10) is determined by the condition $Bx \ll 1$. For neon and argon $B \sim \pm 10^{-29}$ m^3, so that at $x = 10^{25}$ m^{-3} the condition is well met.

Unlike other cases, with the exception of the van der Waals gas discussed in the next section, in a real gas there is a force interaction between the molecules. Due to this, the total pressure P and entropy S of the mixture are no longer the sum of the corresponding values of the individual gases occupying the same volume. However, as will be shown in the Appendix, within the accuracy with which the equation of state (10) is valid, these quantities can be considered additive.

As in the case of perfect gases, here and further we will consider isothermal mixing. It is important that the temperature is the same at the beginning and end of the process. With reversible mixing, the temperature is constant along the entire transition. All calculations except those related to the degenerate Fermi gas were carried out at 300 K.

Unlike perfect gases, for gases with the equation of state (10) it is impossible to ensure equality $P_1^{(i)} = P_2^{(i)}$ of the initial pressures of different gases at equal concentrations. Indeed, the equation

$$B_1 x_1^{\,2} + x_1 = B_2 x_2^{\,2} + x_2 \tag{11}$$

is satisfied only when $B_1 = B_2$, which is possible only for identical gases. Considering (11) as a quadratic equation for x_2, and discarding the physically unacceptable solution, we find the required relationship between concentrations:

$$x_2 = \frac{\sqrt{1 + 4B_2(B_1 x_1^{\,2} + x_1)} - 1}{2B_2}. \tag{12}$$

Let the initial concentration for neon be $x_1 = 10^{25}$ m^{-3}, equal in order of magnitude to the gas concentration at room temperature and a pressure of 1 atm = 101 325 Pa. Then for argon, according to (16), $x_2 = 1.00051 \times 10^{25}$ m^{-3}. The difference from x_1 is small due to the slight deviation of gases from ideality. Then $\Delta P = 0.000021$ atm, which is also small in comparison with the absolute initial pressure, rounded 0.4 atm (Table 4). The same table shows the absolute initial and final entropy and its change $\Delta S = S^{(f)} - S^{(i)} = 5.29330$ J K^{-1}.

Let now the gases be identical ($B_1 = B_2$). Then, for $x_1 = x_2 = x$, using the corresponding formula from Table S2 (ESI†) we find: $\Delta P = P^{(f)} - P^{(i)} = -2\lambda(1 - \lambda)TBx^2$, *i.e.* the final pressure in the vessel is less than the initial pressure even with equal concentrations of identical gases. The initial and final entropy values, taking into account the fact that $B + TB' = b$ (one of the parameters of the van der Waals equation, see Table 1), are equal

$$S^{(i)} = S_B^{(i)} - N_1 bx - N_2 bx, \tag{13}$$

$$S^{(f)} = S_B^{(f)} - Nbx. \tag{14}$$

Since, as established in the previous section, $\Delta S_B = 0$, it follows that $\Delta S = 0$. Thus, in this case, too, no paradox arises if the correct expression for finite entropy is used.

Table 4 Numerical data characterizing the mixing of two gases in a vessel of a fixed volume at 300 K, N = 1 mol, V_2/V_1 = 2

Number of particles		Concentration, m^{-3}		Pressure, atm			Entropy, $J\ K^{-1}$		
N_1	N_2	N_1/V_1	N_2/V_2	$P^{(i)}$	$P^{(f)}$	ΔP	$S^{(i)}$	$S^{(f)}$	ΔS
2.00733×10^{23}	4.01467×10^{23}	1.00000×10^{25}	1.00000×10^{25}	0.408882	0.408882	0	159.471	164.764	5.29349
2.00733×10^{23}	4.01536×10^{23}	1.00000×10^{25}	1.00051×10^{25}	0.408940	0.408961	0.000021	159.483	164.776	5.29330
2.00665×10^{23}	4.01535×10^{23}	1.00000×10^{25}	1.00051×10^{25}	0.408940	0.408961	0.000021	159.465	164.759	5.29435
1.20406×10^{22}	5.90159×10^{23}	1.00000×10^{27}	2.45071×10^{28}	230.831	168.163	−62.668	0	0	0
1.34937×10^{23}	4.67263×10^{23}	9.42828×10^{25}	1.63243×10^{26}	6.6773	6.6773	0	58.796	64.809	6.01325

Almost degenerate e-gas + μ-gas at the beginning of degeneracy

5. Mixing of gases obeying the van der Waals equation

This equation describes well only fairly rarefied gases. Unlike the virial equation, which is a series expansion in the parameter v_0x (see above), the van der Waals equation

$$P = \frac{NT}{V - Nb} - \frac{N^2a}{V^2} = \frac{Tx}{1 - bx} - ax^2 \tag{15}$$

belongs to the class of interpolation equations with two parameters a and b. Comparing the two equations, it is easy to establish the following connection between the second virial coefficient and the van der Waals parameters: $B(T) = b - a/T$, $B + TB' = b$. The prime signifies the derivative with respect to T. The condition for the applicability of eqn (15) is the inequality $bx \ll 1$. For neon and argon at $x = 10^{25}$ m^{-3}, this condition is satisfied.

As in the previous case, it is always possible to select such gas concentrations in the separated parts of the vessel so that the initial pressures $P_1^{(i)}$ and $P_2^{(i)}$ are equal. To do this, you need to satisfy the equation

$$\frac{Tx_1}{1 - b_1x_1} - a_1{x_1}^2 = \frac{Tx_2}{1 - b_2x_2} - a_2{x_2}^2, \tag{16}$$

which reduces to cubic. From Table 4 it can be seen that at a neon concentration $x_1 = 10^{25}$ m^{-3}, the argon concentration $x_2 = 1.00051 \times 10^{25}$ m^{-3} repeats the result of the previous case with the selected accuracy. The remaining results concerning pressure and entropy are also close to the previous ones. Note that physically acceptable solutions (concentrations) of the system of equations $P_1^{(i)} = P_2^{(i)}$, $P^{(f)} = P^{(i)}$ are of the order 10^{28} m^{-3}, at which the equation of state (15) is inapplicable. It follows that it is impossible to ensure equality of the initial and final pressures.

For identical gases ($a_1 = a_2 = a$, $b_1 = b_2 = b$) according to Table S2 (ESI†) we have:

$$\begin{aligned} S^{(i)} &= S_B^{(i)} + N_1 \ln(1 - bx) + N_2 \ln(1 - bx), \\ S^{(f)} &= S_B^{(f)} + N \ln(1 - bx). \end{aligned} \tag{17}$$

Considering that when identical perfect gases are mixed, no change in entropy occurs ($\Delta S_B = 0$), we find that for the van der Waals gas $\Delta S = 0$.

6. Mixing of completely degenerate Fermi gases

As quantum gases, we will choose an electron gas and a gas consisting of muons (μ-mesons in the old terminology). The mass of a muon is approximately 206 times the mass of an electron. Otherwise, the particles do not differ, in particular, both have spin 1/2. The presence of a charge does not interest us, since we neglect the energy of the Coulomb interaction between gas particles. We are also distracted from the fact that the muon is an unstable particle with a half-life of $\sim 10^{-6}$ s. Electron gas is a very real substance present in metals and

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semimetals. In good metal conductors (Cu, Ag) the electron concentration is $\sim 10^{28}$ m^{-3}.

The Fermi gas is completely degenerate at $T = 0$ K, while its entropy, in full accordance with the third law of thermodynamics, is zero (the gas is in one single microstate), therefore the question of the entropy of isothermal mixing of different gases is trivial: $\Delta S = 0$. Indeed, the force interaction of particles is negligible, and the exchange interaction takes place only between identical particles, therefore, in a mixture, gases behave as if there was no other gas. In this regard, there is a clear analogy with a mixture of perfect gases.

As already noted, the Fermi gas exerts pressure on the walls of the container even at absolute zero temperature. This is clear from the fact that (two) particles located at the main (lower) level have zero energy, and therefore zero momentum. The rest are forced to occupy higher levels, hence have momentum and create pressure. Equality of initial pressures can always be ensured by selecting gas concentrations so that the equality $\sigma_1 {x_1}^{5/3} = \sigma_1 {x_1}^{5/3}$ is satisfied, from which the relationship follows

$$\frac{x_2}{x_1} = \left(\frac{\sigma_1}{\sigma_2}\right)^{3/5}. \tag{18}$$

Let us analyze the possibility of isobaric mixing of gases. Taking into account (18), using the formulas given in the corresponding tables, we obtain the equation

$$\begin{aligned} P^{(\mathrm{f})} &= P_1^{(\mathrm{f})} + P_2^{(\mathrm{f})} = \frac{1}{5}\left[\left(\frac{1}{1+A}\right)^{5/3} + \left(\frac{A}{1+A}\right)^{5/3}\right]\sigma_1 {x_1}^{5/3} \\ &= P^{(\mathrm{i})}\left[\frac{1+A^{5/3}}{(1+A)^{5/3}}\right]. \end{aligned} \tag{19}$$

To satisfy the equality $\Delta P = P^{(\mathrm{f})} - P^{(\mathrm{i})} = 0$, it is necessary that the factor in square brackets for $P^{(\mathrm{i})}$ in (19) be equal to one, that is, $1 + A^{5/3} = (1 + A)^{5/3}$. Temporarily denoting $A^{1/3} = \xi$, we obtain equation $1 + \xi^5 - (1 + \xi^3)^5 = 0$, with $0 < \xi < 1$. This equation can be transformed to the form $\xi^{12} + 5(\xi^3 + 1)(\xi^6 + \xi^3 + 1) = \xi^2$. Obviously, it has no positive solutions. In fact, the left side of the equation is obviously >5, and the right side <1. A numerical solution using Wolfram Mathematica 10.4[15] shows that there are only two real roots and both are negative: $\xi_1 = -1$, $\xi_2 = -1.30627\ldots$.

Thus, the pressure in the gas mixture at the end of the process cannot be equal to the initial pressure in pure gases (while maintaining temperature). For the case of the system {e-gas + μ-gas} with initial concentrations of 10^{27} m^{-3} and 2.45×10^{28} m^{-3}, respectively (ensuring equality of initial pressures), before mixing the pressure is 230.8 atm, and decreases by 62.7 atm after mixing (see Table 4).

7. Mixing of almost degenerate Fermi gases

It is almost impossible to find a real case where both mixed gases would be in a state close to degeneracy. This state is realized under the condition $T \ll T_{0\mathrm{F}}$ – the gas temperature must be significantly lower than the degeneracy temperature:

$$T \ll \frac{1}{2}\left(\frac{6\pi^2}{g}\right)^{2/3}\frac{\hbar^2}{m}\left(\frac{N}{V}\right)^{2/3}. \tag{20}$$

Electron gas in metals at $T = 300$ K is such an example: at a concentration $N/V = 10^{27}$ m^{-3} (noticeably lower than the actual one) $T_{0\mathrm{F}} = 4234$ K, which is an order of magnitude higher than room temperature. In reality, it can reach several tens of thousands of degrees. Under these conditions, only a small fraction of electrons have energies above ε_{F}.

If we introduce the notation ${x_{\mathrm{i}}}^{1/3} = z_{\mathrm{i}}$, then the equality of gas pressures before mixing is determined by the equation

$$3(\sigma_1 {z_1}^5 - \sigma_2 {z_2}^5) + 5T^2(\rho_1 z_1 - \rho_2 z_2) = 0. \tag{21}$$

Its numerical solution makes sense only in the case when the gases have comparable degrees of degeneracy. Otherwise, it will be purely formal. We only point out that the pressure of an electron gas with a concentration of 10^{27} m^{-3} will be 235.6 atm; this is about 5 atm higher than for a completely degenerate gas. Note that if this gas hypothetically remained perfect, then at the same temperature its pressure would be equal to 40.9 atm.

Consider the case when the gases are the same ($\sigma_1 = \sigma_2 = \sigma$, $\rho_1 = \rho_2 = \rho$). Naturally, the degrees of degeneracy are also the same. Then eqn (21) is significantly simplified:

$$3\sigma({z_1}^5 - {z_2}^5) + 5\rho T^2(z_1 - z_2) = 0. \tag{22}$$

On the left side you can select the factor $(z_1 - z_2)$:

$$(z_1 - z_2)[3\sigma({z_1}^4 + {z_1}^3 z_2 + {z_1}^2 {z_2}^2 + z_1 {z_2}^3 + {z_2}^4) + 5\rho T^2] = 0. \tag{23}$$

The second factor is obviously positive, therefore the solutions to eqn (23) are $z_1 - z_2 = 0$, that is $x_1 = x_2 = x$. Then the formulas for the initial and final entropy will look like:

$$S^{(\mathrm{i})} = (N_1 + N_2)\rho T x^{-2/3}, \tag{24}$$

$$\begin{aligned} S^{(\mathrm{f})} &= N\left(\frac{N}{V_1 + V_2}\right)\rho T x^{-2/3} \\ &= N\left(\frac{x + Ax}{1 + A}\right)\rho T x^{-2/3} = (N_1 + N_2)\rho T x^{-2/3}. \end{aligned} \tag{25}$$

That is, $S^{(\mathrm{f})} = S^{(\mathrm{i})}$ and $\Delta S = 0$. This was to be expected, since the expression for entropy (and other formulas) was obtained by consistent use of quantum statistics, which takes into account the identity of quantum states arising from any permutations of indistinguishable particles. Artificial division by $N!$, as was necessary to correct the results of classical statistics, is not required.

8. Mixing of Fermi gases at the beginning of degeneracy

This case can be said to be the opposite of the previous one – both gases slightly deviate from Boltzmann behaviour, and not

from purely quantum behaviour. However, the situation with real examples is similar to the previous one, since only hypothetical gases that are simultaneously in the state under consideration can be proposed.

To find the relationship between the initial concentrations of gases at which $P_1^{(i)} = P_2^{(i)}$ it is necessary to solve the quadratic equation

$$(\kappa_1 {x_1}^2 - \kappa_2 {x_2}^2)T^{-3/2} + (x_1 - x_2) = 0. \quad (26)$$

It is clear that such concentrations can always be selected, and in order for the equality $P^{(f)} = P^{(i)}$ to hold, the equation must be satisfied

$$T(x_2 - x_1) - (1 + \lambda)T^{-1/2}\kappa_1 {x_1}^2 + (1 - \lambda)T^{-1/2}\kappa_2 {x_2}^2 = 0. \quad (27)$$

But since from (29) it follows

$$T(x_2 - x_1) = T^{-1/2}(\kappa_1 {x_1}^2 - \kappa_2 {x_2}^2),$$

we get

$$[(1 - \lambda) + \lambda^2 - 1]\kappa_1 {x_1}^2 + [(1 - \lambda)^2 - (1 - \lambda)]\kappa_2 {x_2}^2 = 0. \quad (28)$$

Both square brackets are equal to $\lambda(\lambda - 1)$, so (27) reduces to the equation

$$\kappa_1 {x_1}^2 + \kappa_2 {x_2}^2 = 0, \quad (29)$$

which has no real solutions, so isobaric mixing is impossible.

When the gases are identical ($\kappa_1 = \kappa_2$), eqn (26) takes the form

$$(x_1 - x_2)[1 + \kappa T^{-3/2}(x_1 + x_2)] = 0, \quad (30)$$

from which it follows $x_1 = x_2 = x$. Then

$$\begin{aligned} S^{(i)} &= S_B^{(i)} + \frac{1}{2}\kappa(N_1 + N_2)T^{-3/2}x, \\ S^{(f)} &= S_B^{(f)} + \frac{1}{2}\kappa(N_1 + N_2)\frac{1 + A}{1 + A}T^{-3/2}x = S^{(i)}. \end{aligned} \quad (31)$$

that is, we again come to a zero change in entropy and compliance with the third law of thermodynamics.

9. Mixing of Fermi gases in different degrees of degeneracy

Mixing e-gas with μ-gas is just such a case. Due to the difference in particle masses, the degeneration temperatures of these gases are significantly different. At the chosen concentration of 10^{27} m^{-3} for electrons $T_{0F} = 4234$ K, for muons – 20.5 K, therefore at 300 K the e-gas differs slightly from the degenerate gas, and the μ-gas differs slightly from the Boltzmann gas.

As always, we start by finding out whether it is possible to have equal gas pressures before mixing. We write out the corresponding equation:

$$\frac{1}{5}\sigma_1 {x_1}^{5/3} + \frac{1}{3}T^2\rho_1 {x_1}^{1/3} = Tx_2 + T^{-1/2}\kappa_2 {x_2}^2. \quad (32)$$

Obviously, eqn (32) can always be satisfied, but it turns out that it is compatible with the equation $\Delta P = P^{(f)} - P_1^{(i)} = 0$, which has the form

$$\begin{aligned} &\frac{1}{5}\left(\lambda^{5/3} - 1\right)\sigma_1 {x_1}^{5/3} + \frac{1}{3}\left(\lambda^{1/3} - 1\right)T^2\rho_1 {x_1}^{1/3} \\ &\quad + (1 - \lambda)Tx_2 + (1 - \lambda)^2 T^{-1/2}\kappa_2 {x_2}^2 = 0. \end{aligned} \quad (33)$$

Numerically solving system (32) and (33) using Mathematica 10.4[15] with respect to concentrations gives $x_1(e) = 9.43 \times 10^{25}$ m^{-3}, $x_2(\mu) = 1.63 \times 10^{26}$ m^{-3}. Thus, in this case, the mixing of gases can be isobaric. The initial and final pressure turns out to be 6.68 atm. With new concentrations, the degeneracy temperatures change: $T_{0F}(e) = 877$ K, $T_{0F}(\mu) = 6.1$ K. As can be seen, the μ-gas approaches the Boltzmann regime more closely, and the e-gas becomes less degenerate. Despite this, the formulas describing the thermodynamic functions of an almost degenerate gas remain quite accurate. The entropy of mixing ΔS_{per} 1 mole of the total amount of gases turned out to be equal to 6.01 J K^{-1}. Other results can be found in Table 4.

Additionally, we have derived formulas that can be used, if necessary, to calculate mixing functions for entropy and internal energy for all types of gases, as well as temperature and pressure jumps under conditions other than those adopted in this work. These results are summarized in Table S3 (ESI†).

10. Conclusions

Equality of initial pressures of mixed unequal gases cannot always be ensured at arbitrary volumetric concentrations, but only at their certain ratios. But even if this requirement is met, isothermal mixing cannot be carried out without changing the total pressure and, as a consequence, the thermodynamic effects of mixing cannot be directly compared with the case of perfect gases. In the case of quantum gases, one of which is almost degenerate and the other weakly degenerate, isobaric–isothermal mixing is possible.

With the consistent application of quantum statistics, no paradoxes arise that are characteristic of a smooth transition from different gases to identical ones. The obtained thermodynamic relationships allow you to calculate the thermal and other effects of reversible and irreversible mixing.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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