Section S1. Additional tables

Table S1. Thermodynamic functions of gases in various states

	Ideal (Boltzmann) gas	Rarefied real gas	Van der Waals gas	Degenerate Fermi gas	Almost degenerate Fermi gas	Fermi gas at the beginning of degeneracy
Energy, U	$U_B = \frac{3}{2}NT$	$U_B - NT^2 B'x$	$U_B - Nax$	$U_0 = \frac{3}{10}\sigma Nx^{2/3}$	$U_0 + \frac{1}{2}\rho T^2 Nx^{-2/3}$	$U_B + \frac{3}{2}\kappa NT^{-1/2}x$
Enthalpy, H	$H_B = \frac{5}{2}NT$	$H_B + NT(B - TB')x$	$H_B + NT\frac{bx}{1-bx} - 2Nax$	$H_0 = \frac{1}{2}\sigma Nx^{2/3}$	$H_0 + \frac{5}{6}\rho T^2 Nx^{-2/3}$	$H_B + \frac{5}{2}\kappa NT^{-1/2}x$
Helmholtz energy, F	$F_B = NT\ln\frac{xV_Q}{eg}$	$F_B + NTBx$	$F_B - NT\ln(1-bx) - Nax$	$F_0 = \frac{3}{10}\sigma Nx^{2/3}$	$F_0 - \frac{1}{2}\rho T^2 Nx^{-2/3}$	$F_B + \kappa NT^{-1/2}x$
Gibbs energy, G	$G_B = NT\ln\frac{xV_Q}{g}$	$G_B + 2NTBx$	$G_B + NT\left[\frac{bx}{1+bx} - \ln(1-bx)\right] - 2Nax$	$G_0 = \frac{1}{2}\sigma Nx^{2/3}$	$G_0 - \frac{1}{6}\rho T^2 Nx^{-2/3}$	$G_B + 2\kappa NT^{-1/2}x$
Chemical potential, μ	$\mu_B = T\ln\frac{xV_Q}{g}$	$\mu_B + 2TBx$	$\mu_B + T\left[\frac{bx}{1+bx} - \ln(1-bx)\right] - 2ax$	$\mu_0 = \frac{1}{2}\sigma x^{2/3}$	$\mu_0 - \frac{1}{6}\rho T^2 x^{-2/3}$	$\mu_B + 2\kappa T^{-1/2}x$
Ω-potential,	$\Omega_B = -NT$	$\Omega_B - NTBx$	$\frac{\Omega_B}{1-bx} + Nax$	$\Omega_0 = -\frac{1}{5}\sigma Nx^{2/3}$	$\Omega_0 - \frac{1}{3}\rho T^2 Nx^{-2/3}$	$\Omega_B + \frac{N}{32g\kappa}T^{5/2}V_Q^2 T^{5/2}x$
Entropy, S	$S_B = -N\ln\frac{xV_Q}{g} + \frac{5}{2}N$	$S_B - N(B + TB')x$	$S_B + N\ln(1-bx)$	$S_0 = 0$	$S = \rho TNx^{-2/3}$	$S_B + \frac{1}{2}\kappa NT^{-3/2}x$
Isochoric heat capacity, C	$C_B = \frac{3}{2}N$	$C_B - NT(2B' + TB'')x$	C_B	$C_0 = 0$	$C = \rho TNx^{-2/3}$	$C_B - \frac{3}{4}\kappa NT^{-3/2}x$
Heat of volume change, l	$l_B = Tx$	$l_B + T(B + TB')x^2$	$\frac{l_B}{1-bx}$	$l_0 = 0$	$l = \frac{2}{3}\rho T^2 x^{1/3}$	$l_B - \frac{1}{2}\kappa T^{-1/2}x^2$
Pressure, P	$P_B = Tx$	$T(1 + Bx)x$	$\frac{P_B}{V-bx} - ax^2$	$P_0 = \frac{1}{5}\sigma x^{5/3}$	$P_0 + \frac{1}{3}\rho T^2 x^{1/3}$	$P_B + \kappa T^{-1/2}x^2$
Thermal expansion coefficient, α	$\alpha_B = \frac{1}{T}$	$\alpha_B\frac{1+Bx}{1+2Bx}$	$\frac{1-bx}{T-2a(1-bx)^2 x}$	$\alpha_0 = 0$	$\frac{6T}{\frac{3\sigma}{\rho}x^{4/3} + T^2}$	$\alpha_B\frac{1 - \frac{1}{2}\kappa T^{-3/2}x}{1 + 2\kappa T^{-3/2}x}$

Compressibility factor, β	$\beta_B = \dfrac{1}{xT}$	$\dfrac{\beta_B}{1+2Bx}$	$\dfrac{(1-bx)^2}{Tx - 2a(1-bx)^2 x^2}$	$\beta_0 = \dfrac{3}{\sigma} x^{-5/3}$	$\dfrac{\frac{9}{\rho}x^{-1/3}}{\frac{3\sigma}{\rho}x^{4/3} + T^2}$	$\dfrac{\beta_B}{1+2\kappa T^{-3/2}x}$
Pressure coefficient, γ	$\gamma_B = \dfrac{1}{T}$	$\gamma_B\dfrac{1+(B+TB')x}{1+Bx}$	$\dfrac{1}{T - a(1-bx)x}$	$\gamma_0 = 0$	$-\dfrac{10T}{\frac{3\sigma}{\rho}x^{4/3} + 5T^2}$	$\gamma_B\dfrac{1-\frac{1}{2}\kappa T^{-3/2}x}{1+\kappa T^{-3/2}x}$

Table S2. Working formulas and some notations

Ideal gases	$P^{(i)}$	$Tx_1, \quad Tx_2$	Almost degenerate Fermi gases	$P^{(i)}$	$\frac{1}{5}\sigma_1 x_1^{5/3} + \frac{1}{3}\rho_1 T^2 x_1^{1/3}, \quad \frac{1}{5}\sigma_2 x_2^{5/3} + \frac{1}{3}\rho_2 T^2 x_2^{1/3}$
	$P^{(f)}$	$T[\lambda x_1 + (1-\lambda)x_2]$		$P^{(f)}$	$\frac{1}{5}\lambda^{5/3}\sigma_1 x_1^{5/3} + \frac{1}{3}\lambda^{1/3}\rho_1 T^2 x_1^{1/3} + \frac{1}{5}(1-\lambda)^{5/3}\sigma_2 x_2^{5/3} + \frac{1}{3}(1-\lambda)^{1/3}\rho_2 T^2 x_2^{1/3}$
	ΔP	$T(1-\lambda)(x_2 - x_1), \quad -T\lambda(x_2 - x_1)$		ΔP	$\frac{1}{5}(\lambda^{5/3}-1)\sigma_1 x_1^{5/3} + \frac{1}{3}(\lambda^{1/3}-1)\rho_1 T^2 x_1^{1/3} + \frac{1}{5}(1-\lambda)^{5/3}\sigma_2 x_2^{5/3} + \frac{1}{3}(1-\lambda)^{1/3}\rho_2 T^2 x_2^{1/3}$
	$S^{(i)}$	$N_1\left(-\ln\dfrac{x_1 V_{Q1}}{g_1} + \dfrac{5}{2}\right) + N_2\left(-\ln\dfrac{x_2 V_{Q2}}{g_2} + \dfrac{5}{2}\right)$		$S^{(i)}$	$T[\rho_1 N_1 x_1^{-2/3} + \rho_2 N_2 x_2^{-2/3}]$
	$S^{(f)}$	$N_1\left(-\ln\dfrac{\lambda x_1 V_{Q1}}{g_1} + \dfrac{5}{2}\right) + N_2\left[-\ln\dfrac{(1-\lambda)x_2 V_{Q2}}{g_2} + \dfrac{5}{2}\right]$		$S^{(f)}$	$T[\rho_1 N_1 \lambda^{-2/3} + \rho_2 N_2 (1-\lambda)^{-2/3}]$
	ΔS	$-N_1\ln\lambda - N_2\ln(1-\lambda)$		ΔS	$\rho_1 N_1 T(\lambda^{-2/3}-1)x_1^{-2/3} + \rho_2 N_2 T[(1-\lambda)^{-2/3}-1]x_2^{-2/3}$
Rarefied real gases	$P^{(i)}$	$T(B_1 x_1^2 + x_1), \quad P_2^{(i)} = T(B_2 x_2^2 + x_2)$	Fermi gases at the beginning of degeneracy	$P^{(i)}$	$x_1 T + \kappa_1 x_1^2 T^{-1/2}, \quad x_2 T + \kappa_2 x_2^2 T^{-1/2}$
	$P^{(f)}$	$T[\lambda x_1 + B_1\lambda^2 x_1^2 + (1-\lambda)x_2 + B_2(1-\lambda)^2 x_2^2]$		$P^{(f)}$	$\lambda T x_1 + \lambda T x_2 + \lambda^2 \kappa_1 x_1^2 T^{-1/2} + (1-\lambda)^2 \kappa_2 x_2^2 T^{-1/2}$
	ΔP	$-(1-\lambda)T[(x_1 - x_2) + (1+\lambda)B_1 x_1^2 - (1-\lambda)B_2 x_2^2]$		ΔP	$(1-\lambda)(x_2 - x_1)T + (\lambda^2 -1)\kappa_1 x_1^2 T^{-1/2} + (1-\lambda)^2 \kappa_2 x_2^2 T^{-1/2}$

		Van der Waals gases	Fermi gas at different degrees of degeneracy		
	$S^{(i)}$	$S_B^{(i)} - N_1 b_1 x_1 - N_2 b_2 x_2$		$S^{(i)}$	$S_B^{(i)} + \frac{1}{2}\left(\kappa_1 N_1 x_1 + \kappa_2 N_2 x_2\right)T^{-3/2}$
	$S^{(f)}$	$S_B^{(f)} - N_1 b_1 \lambda x_1 - N_2 b_2 (1-\lambda) x_2$		$S^{(f)}$	$S_B^{(f)} + \frac{1}{2}[\kappa_1 N_1 \lambda x_1 + \kappa_2 N_2 (1-\lambda) x_2]T^{-3/2}$
	ΔS	$\Delta S_B + N_1 b_1 \lambda A x_1 + N_2 b_2 \lambda x_2$		ΔS	$\Delta S_B - \frac{1}{2}[(1-\lambda)\kappa_1 N_1 x_1 + \lambda \kappa_2 N_2 x_2]T^{-3/2}$
Van der Waals gases	$P^{(i)}$	$\frac{Tx_1}{1-b_1 x_1} - a_1 x_1^2, \quad \frac{Tx_2}{1-b_2 x_2} - a_2 x_2^2$	Fermi gas at different degrees of degeneracy	$P^{(i)}$	$\frac{1}{5}\sigma_1 x_1^{5/3} + \frac{1}{3}T^2 \rho_1 x_1^{1/3}, \quad Tx_2 + T^{-1/2}\kappa_2 x_2^2$
	$P^{(f)}$	$\frac{\lambda Tx_1}{1-\lambda b_1 x_1} + \frac{(1-\lambda)Tx_2}{1-(1-\lambda)b_2 x_2} -$ $-\lambda^2 a_1 x_1^2 - (1-\lambda^2)a_2 x_2^2$		$P^{(f)}$	$\frac{1}{5}\lambda^{5/3}\sigma_1 x_1^{5/3} + \frac{1}{3}\lambda^{1/3}T^2 \rho_1 x_1^{1/3} +$ $+ (1-\lambda)Tx_2 + (1-\lambda)^2 T^{-1/2}\kappa_2 x_2^2$
	ΔP	$-\frac{(1-\lambda)Tx_1}{(1-\lambda b_1 x_1)(1-b_1 x_1)} + \frac{(1-\lambda)Tx_2}{1-(1-\lambda)b_2 x_2} +$ $+\frac{1-\lambda^2}{\lambda}a_1 x_1^2 - (1-\lambda)^2 a_2 x_2^2$		ΔP	$\frac{1}{5}(\lambda^{5/3}-1)\sigma_1 x_1^{5/3} + \frac{1}{3}(\lambda^{1/3}-1)T^2 \rho_1 x_1^{1/3} +$ $+ (1-\lambda)Tx_2 + (1-\lambda)^2 T^{-1/2}\kappa_2 x_2^2$
	$S^{(i)}$	$S_B^{(i)} + N_1 \ln(1-b_1 x_1) +$ $+ N_2 \ln(1-b_2 x_2)$		$S^{(i)}$	$T\rho_1 N_1 x_1^{-2/3} - N_2\left(\ln\frac{V_{Q2}x_2}{g_2} - \frac{5}{2} - \frac{1}{2}T^{-3/2}\kappa_2 x_2\right)$
	$S^{(f)}$	$_B^{(f)} + N_1 \ln(1-\lambda b_1 x_1) +$ $+ N_2 \ln[1-(1-\lambda)b_2 x_2]$		$S^{(f)}$	$\lambda^{-2/3}T\rho_1 N_1 x_1^{-2/3} - N_2 \ln\left[\frac{(1-\lambda)V_{Q2}x_2}{g_2}\right] + \frac{5}{2}N_2 +$ $+ \frac{1}{2}(1-\lambda)T^{-3/2}\kappa_2 N_2 x_2$
	ΔS	$\Delta S_B + N_1 \ln\left(\lambda + \frac{1-\lambda}{1-b_1 x_1}\right) + + N_2 \ln\left(\frac{1-\lambda}{\lambda} + \frac{1}{1-b_2 x_2}\right)$		ΔS	$(\lambda^{-2/3}-1)T\rho_1 N_1 x_1^{-2/3} - N_2 \ln(1-\lambda) - -\frac{1}{2}(1-\lambda)T^{-3/2}\kappa_2 N_2 x_2$
Completely degenerate Fermi gases	$P^{(i)}$	$\frac{1}{5}\sigma_1 x_1^{5/3}, \quad \frac{1}{5}\sigma_2 x_2^{5/3}$			
	$P^{(f)}$	$\frac{1}{5}\lambda^{5/3}\sigma_1 x_1^{5/3} + \frac{1}{5}(1-\lambda)^{5/3}\sigma_2 x_2^{5/3}$			

	ΔP	$\dfrac{1}{5}[\lambda^{5/3} + (1-\lambda)^{5/3} - 1]\sigma_1 x_1^{5/3}$			

Notations: $\dfrac{V_2}{V_1} = A,\quad \dfrac{1}{1+A} = \lambda,\quad N = N_1 + N_2,\quad \dfrac{N_1}{V_1} = x_1,\quad \dfrac{N_2}{V_2} = x_2,\quad \dfrac{N_1}{N_2} = \dfrac{1}{A}\dfrac{x_1}{x_2},\quad N_1 = N\left(1 + A\dfrac{x_2}{x_1}\right)^{-1},\quad N_2 = N\left(1 + \dfrac{1}{A}\dfrac{x_1}{x_2}\right)^{-1},\quad \dfrac{N_1}{V} = \dfrac{1}{1+A}x_1,\quad \dfrac{N_2}{V} = \dfrac{A}{1+A}x_2$

Table S3. Formulas for calculating changes in temperature, pressure, energy and entropy during reversible mixing of gases under various conditions

Thermodynamic formula	Ideal gas	Rarefied real gas	Degenerate Fermi gas	Almost degenerate Fermi gas	Fermi gas at the beginning of degeneracy
$\left(\dfrac{\partial T}{\partial V}\right)_P = \dfrac{1}{\alpha V}$	$\dfrac{T}{V}$	$\dfrac{T}{V}\dfrac{1 + 2B\dfrac{N}{V}}{1 + B\dfrac{N}{V}}$	∞	$\dfrac{\sigma}{2\rho TV}\left(\dfrac{N}{V}\right)^{4/3} + \dfrac{T}{6V}$	$\dfrac{T}{V}\dfrac{1 + 2\kappa T^{-3/2}\left(\dfrac{N}{V}\right)}{1 - \dfrac{1}{2}\kappa T^{-3/2}\left(\dfrac{N}{V}\right)}$
$\left(\dfrac{\partial T}{\partial V}\right)_U = \dfrac{1}{C}P(1 - \gamma T)$	0	$-\dfrac{2}{3}\dfrac{T^2}{V}B'\dfrac{N}{V}$	∞	$\dfrac{\sigma}{5\rho TV}\left(\dfrac{N}{V}\right)^{4/3} - \dfrac{T}{3V}$	$\dfrac{1}{N}\dfrac{\kappa T^{-1/2}\left(\dfrac{N}{V}\right)^2}{1 - \dfrac{\kappa}{2}T^{-3/2}\left(\dfrac{N}{V}\right)}$
$\left(\dfrac{\partial T}{\partial V}\right)_S = -\dfrac{\gamma TP}{C}$	$-\dfrac{2}{3}\dfrac{T}{V}$	$-\dfrac{2}{3}\dfrac{T}{V}\left[1 + (B + TB')\dfrac{N}{V}\right]$	∞	$\dfrac{\sigma}{2\rho TV}\left(\dfrac{N}{V}\right)^{4/3} + \dfrac{T}{6V}$	$-\dfrac{2}{3}\dfrac{T}{V}$
$\left(\dfrac{\partial P}{\partial V}\right)_T = -\dfrac{1}{\beta V}$	$-\dfrac{NT}{V^2}$	$-\dfrac{NT}{V^2}\left(1 + 2B\dfrac{N}{V}\right)$	$-\dfrac{\sigma}{3V}\left(\dfrac{N}{V}\right)^{5/3}$	$-\dfrac{\sigma}{3V}\left(\dfrac{N}{V}\right)^{5/3} - \dfrac{\rho T^2}{9V}\left(\dfrac{N}{V}\right)^{1/3}$	$-\dfrac{NT}{V^2}\left[1 + 2\kappa T^{-3/2}\left(\dfrac{N}{V}\right)\right]$
$\left(\dfrac{\partial P}{\partial V}\right)_U = \dfrac{1}{C}\gamma P^2(1 - \gamma T) - \dfrac{1}{\beta V}$	$-\dfrac{NT}{V^2}$	$-\dfrac{NT}{V^2}\left\{1 + 2B\dfrac{N}{V} + \dfrac{2}{3}\dfrac{N}{V}TB'\left[1 + (B + TB')\dfrac{N}{V}\right]\right\}$	$-\dfrac{\sigma}{5V}\left(\dfrac{N}{V}\right)^{5/3}$	$-\dfrac{\sigma}{5V}\left(\dfrac{N}{V}\right)^{5/3} - \dfrac{\rho T^2}{3V}\left(\dfrac{N}{V}\right)^{1/3}$	$-\dfrac{NT}{V^2}\left[1 + \kappa T^{-3/2}\left(\dfrac{N}{V}\right)\right]$
$\left(\dfrac{\partial P}{\partial V}\right)_S = -\dfrac{1}{C}T\gamma^2 P^2 - \dfrac{1}{\beta V}$	$-\dfrac{5}{3}\dfrac{NT}{V^2}$	$-\dfrac{NT}{V^2}\left\{1 + 2B\dfrac{N}{V} + \dfrac{2}{3}\left[1 + (B + TB')\dfrac{N}{V}\right]^2\right\}$	$-\dfrac{\sigma}{3V}\left(\dfrac{N}{V}\right)^{5/3}$	$-\dfrac{\sigma}{3V}\left(\dfrac{N}{V}\right)^{5/3} - \dfrac{5\rho T^2}{9V}\left(\dfrac{N}{V}\right)^{1/3}$	$-\dfrac{5}{3}\dfrac{NT}{V^2}\left[1 + \kappa T^{-3/2}\left(\dfrac{N}{V}\right)\right]$
$\left(\dfrac{\partial U}{\partial V}\right)_T = -P(1 - \gamma T)$	0	$T^2 B'\left(\dfrac{N}{V}\right)^2$	$-\dfrac{\sigma}{5}\left(\dfrac{N}{V}\right)^{5/3}$	$-\dfrac{\sigma}{5}\left(\dfrac{N}{V}\right)^{5/3} + \dfrac{\rho T^2}{3}\left(\dfrac{N}{V}\right)^{1/3}$	$\dfrac{3\kappa}{2}T^{-1/2}\left(\dfrac{N}{V}\right)^2$

$\left(\dfrac{\partial U}{\partial V}\right)_P = \dfrac{C}{\beta\gamma PV} - P(1-\gamma T) = \dfrac{3}{2}P$	$\dfrac{3}{2}\dfrac{NT}{V}$	$\dfrac{3}{2}\dfrac{NT}{V}\dfrac{\left(1+2B\dfrac{N}{V}\right)}{1+(B+TB')\dfrac{N}{V}} - \dfrac{N^2T^2}{V^2}B'$	$\dfrac{3\sigma}{10}\left(\dfrac{N}{V}\right)^{5/3}$	$\dfrac{3\sigma}{10}\left(\dfrac{N}{V}\right)^{5/3} + \dfrac{\rho T^2}{2}\left(\dfrac{N}{V}\right)^{1/3}$	$\dfrac{3}{2}\dfrac{NT}{V}\left[1+\kappa T^{-3/2}\left(\dfrac{N}{V}\right)\right]$
$\left(\dfrac{\partial U}{\partial V}\right)_S = -P$	$-\dfrac{NT}{V}$	$-\dfrac{NT}{V}\left(1+B\dfrac{N}{V}\right)$	$-\dfrac{\sigma}{5}\left(\dfrac{N}{V}\right)^{5/3}$	$-\dfrac{\sigma}{5}\left(\dfrac{N}{V}\right)^{5/3} - \dfrac{\rho T^2}{3}\left(\dfrac{N}{V}\right)^{1/3}$	$-\dfrac{NT}{V}\left[1+\kappa T^{-3/2}\left(\dfrac{N}{V}\right)\right]$
$\left(\dfrac{\partial S}{\partial V}\right)_T = \gamma P$	$\dfrac{N}{V}$	$\dfrac{N}{V}\left[1+(B+TB')\dfrac{N}{V}\right]$	0	$\dfrac{2\rho T}{3}\left(\dfrac{N}{V}\right)^{1/3}$	$\dfrac{N}{V}\left[1-\dfrac{\kappa}{2}T^{-3/2}\left(\dfrac{N}{V}\right)\right]$
$\left(\dfrac{\partial S}{\partial V}\right)_P = \dfrac{C}{\beta V\gamma PT} + \gamma P$	$\dfrac{5}{2}\dfrac{N}{V}$	$\dfrac{3}{2}\dfrac{N}{V}\dfrac{1+2B\dfrac{N}{V}}{1+(B+TB')\dfrac{N}{V}}$	$\dfrac{\sigma}{2T}\left(\dfrac{N}{V}\right)^{5/3}$	$\dfrac{\sigma}{2T}\left(\dfrac{N}{V}\right)^{5/3} + \dfrac{\rho T}{2}\left(\dfrac{N}{V}\right)^{1/3}$	$\dfrac{5}{2}\dfrac{N}{V}\left[1+\kappa T^{-3/2}\left(\dfrac{N}{V}\right)\right]$
$\left(\dfrac{\partial S}{\partial V}\right)_U = \dfrac{P}{T}$	$\dfrac{N}{V}$	$\dfrac{N}{V}\left(1+B\dfrac{N}{V}\right)$	$\dfrac{\sigma}{5T}\left(\dfrac{N}{V}\right)^{5/3}$	$\dfrac{\sigma}{5T}\left(\dfrac{N}{V}\right)^{5/3} + \dfrac{\rho T}{3}\left(\dfrac{N}{V}\right)^{1/3}$	$\dfrac{N}{V}\left[1+\kappa T^{-3/2}\left(\dfrac{N}{V}\right)\right]$

Section S2. Entropy of perfect gases

As is known, the additivity of thermodynamic quantities occurs due to the neglect of the interaction of individual macroscopic parts of the body. For any mixture of substances (at the molecular level), for example, liquids or real gases, the thermodynamic quantities will not be equal to the sums of the corresponding quantities of the individual components. An exception is a perfect gas, since the interaction of its molecules, by definition, can be neglected. Thus, the entropy of a mixture of perfect gases is equal to the sum of the entropies of each of the gases that occupy a volume equal to the volume of the mixture and behave as if there were no other gases.

You can mix two different gases in different ways, but the change in entropy will be the same, since entropy is a function of state, and its change is determined only by the final and initial states. The same is true, of course, for any other state functions. Let us obtain a formula as a function of temperature and volume for the entropy of a perfect gas consisting of a fixed number N of particles of the same type. We start from the fundamental equation $dU = TdS - PdV$, that describes the change in the internal energy of any closed system with a reversible change in the natural variables of a given thermodynamic property. Since according to (2) $dU^{(\text{id})} = C_V dT$, $P = NT/V$, we have (id − *ideal*):

$$dS^{(\text{id})} = \frac{1}{T}dU + \frac{P}{T}dV = C_V \frac{dT}{T} + N\frac{dV}{V}. \tag{S1}$$

Integrating this expression, we find:

$$S^{(\text{id})} = C_V \ln T + N \ln V + \text{const}. \tag{S2}$$

It would be more correct to rewrite expression (4) in the form

$$S^{(\text{id})} = S_0 + C_V \ln \frac{T}{T_0} + N \ln \frac{V}{V_0}, \tag{S3}$$

where S_0 – entropy of a gas having a temperature T_0 and occupying a volume V_0.

It is easy to see that formulas (S2) and (S3) do not correspond to the third law of thermodynamics, according to which the entropy of any equilibrium body tends to zero at $T \to 0$. Indeed, no choice of the integration constant S_0 can obtain the required result. It would be possible to get rid of negative entropy values by unlimitedly increasing the volume of gas, but this still does not make it possible to establish a specific additive constant. The reason is the same – as the absolute temperature tends to zero, the gas inevitably becomes quantum and then degenerate, and equation (1), used in deriving formulas (S2) and (S3), loses its validity. Calculating entropy taking into account quantum behaviour leads to agreement with the third law. To illustrate, we present expressions for the entropy of an almost degenerate Fermi gas of particles with spin ½, for example, an electron gas or a gas consisting of alkali metal atoms with an odd sum of atomic weight and atomic number, and an almost degenerate Bose gas with zero spin, for example, helium [14]:

$$S_{\text{Fermi}} = \left(\frac{\pi}{3}\right)^{2/3} \frac{m}{\mathsf{h}^2} NT \left(\frac{V}{N}\right)^{-2/3}, \qquad S_{\text{Bose}} = \left(\frac{\pi}{3}\right)^{2/3} \frac{m^{3/2}}{\mathsf{h}^3} NT^{3/2}V. \tag{S4}$$

Here m is the particle mass. As it can be seen, in both cases the entropy in the state of complete degeneracy ($T = 0$) is zero.

The calculation of the entropy of a perfect gas, as well as its other thermodynamic quantities, begins in statistical thermodynamics with the calculation of the molecular sum Q over the states of gas particles. The contribution of translational motion, which can always be separated from the contributions of the internal degrees of freedom of the particle, is most convenient and easiest to calculate within the framework of classical statistics, replacing the sum with a statistical integral:

$$Q = \int e^{-\frac{\varepsilon}{T}} dp\,dq = \int e^{-\frac{p_x^2 + p_y^2 + p_z^2}{2mT}} dp_x dq_y dq_z dx\,dy\,dz \,. \tag{S5}$$

This can be done because the translational motion of a particle in a volume of macroscopic dimensions is always quasi-classical. Integration is performed over all possible values of the components of momentum and particle coordinates. Due to the independence of particles, the sum over the states Z of the entire gas must contain the multiplier Q^N.

It is very important that the statistical integral does not take into account the physical identity of the states resulting from any rearrangement of particles. Formally, these states are described by different points in the phase space of the system, that is, they are different classical states. Meanwhile, each state in a sum or integral Z must be taken into account only once. Therefore, it is necessary to artificially divide the product of statistical sums by the total number of permutations of identical particles. If a gas consists of particles without internal degrees of freedom, but having a spin moment with quantum number s, then each energy level of translational motion receives an additional degeneracy with multiplicity $g = 2s + 1$, therefore the factor g should be introduced into the expression for Z. As a result we have

$$Z = \frac{gQ^N}{N!} \,. \tag{S6}$$

It is equally important to note that with a completely quantum approach, the factor $N!$ is taken into account automatically, since rearranging indistinguishable particles does not change the state.

With that said, the quasi-classical approach yields the following expression for the Helmholtz energy:

$$F = -T \ln Z = -NT \ln\left[\frac{egV}{N} \left(\frac{mT}{2\pi\hbar^2} \right)^{3/2} Q_{\text{in}} \right] = -NT \ln\frac{egV}{N} + Nf(T) \,. \tag{S7}$$

In the last formula, term containing the volume is separated, then f is a function of temperature only, which will be known if the partition function Q_{in} associated with the internal degrees of freedom is calculated. If there are no such degrees of freedom, then $Q_{\text{in}} = 1$, and we are dealing with a gas of "elementary particles" with three translational degrees of freedom. In this case of interest to us

$$f(T) = -T \ln\left(\frac{mT}{2\pi\hbar^2} \right)^{3/2} = T \ln V_{\text{Q}} \,. \tag{S8}$$

The quantity V_{Q} is called quantum volume. Its visual physical meaning is that in order of magnitude it is equal to the volume of a cube with an edge equal to the de Broglie wavelength of the particle. For example, at $T = 300$ K for neon $V_{\text{Q}} \approx 10^{-32}$ m^3. It is convenient to express the condition for the applicability of the quasi-classical approximation through the quantum volume:

$$\frac{N}{V} V_{\text{Q}} \ll 1 \,. \tag{S9}$$

At atmospheric pressure and room temperature $N/V \sim 10^{25}$ m^{-3}, the left side of the inequality is of order 10^{-7}, so the condition is well satisfied. That is, the gas is in the Boltzmann regime, which corresponds to a perfect gas. For neon with an atomic concentration of 10^{25} m^{-3}, this regime occurs at $T \square 0.007$ K.

For the entropy of a perfect gas we obtain

$$S = -\left(\frac{\partial F}{\partial T} \right)_V = N \ln\frac{egV}{N} - Nf'(T) = N\left(-\ln\frac{1}{g}\frac{N}{V}V_{\text{Q}} + \frac{5}{2} \right) \,. \tag{S10}$$

The prime indicates the derivative with respect to temperature. At a fixed T, formula (S10) gives the dependence of entropy on the volume concentration N/V of particles in the gas.

Section S3. Accuracy of additivity of partial pressures of rarefied gas components

In this section, we use the practical units of entropy ($J \cdot K^{-1}$) and temperature (K), measure the amounts of substances n_i in moles, and by x_i we mean the mole fraction of component i of the gas mixture. We consider an equilibrium mixture of gases that individually obey equation (14) of the main text. It is convenient to describe the thermodynamic properties of the mixture in the variables T and P, then the Gibbs energy G, for which these variables are natural, should be taken as the initial value. In these variables, property G is a characteristic function from which any other thermodynamic property can be calculated. Our goal is to estimate how much the entropy of a real mixture differs from the entropy of a mixture of perfect gases $S_B = S_{1B} + S_{2B}$.

The Gibbs energy of any binary system is expressed through the chemical potentials of the components by the relation

$$G = n_1\mu_1 + n_2\mu_2. \tag{S11}$$

The chemical potentials of a real gas, according to Lewis, are expressed by the same formula as for a perfect gas, but with pressure P_i replaced by fugacity f_i:

$$\mu_i(T,P) = \mu_i°(T) + RT\ln f_i = \mu_i° + RT\ln P_i + RT\ln\gamma_i = \mu_B + RT\ln\gamma_i, \tag{S12}$$

where $\gamma_i = f_i/P_i$ are the fugacity coefficients, μ_i is the chemical potential of gas i in the standard state, which is taken to be a perfect gas under a pressure of 1 bar = 10^5 Pa. Since the first two terms in (S12) constitute the chemical potentials μ_{iB} of gases in a perfect state, this expression can be rewritten as

$$\mu_i(T,P) = \mu_B(T) + RT\ln\gamma_i(T,P). \tag{S13}$$

To characterize the composition of a binary mixture, one variable $x_2 = x$ is sufficient, then $x_1 = 1 - x$. After passing to the molar Gibbs energy G_m, instead of (S11) we obtain

$$G_m = (1-x)\mu_1 + x\mu_2. \tag{S14}$$

Substituting expressions (S13) into (S14) and moving the terms related to the perfect gas to the left, we will have the excess Gibbs energy:

$$G^E = G - G_{mB} = RT[(1-x)\ln\gamma_1 + x\ln\gamma_2] \tag{S15}$$

Differentiating (S15) by temperature, we find the excess entropy

$$S^E = -\left(\frac{\partial G^E}{\partial T}\right)_{P,x} = -R\left\{(1-x)\left[\ln\gamma_1 + T\left(\frac{\partial\ln\gamma_1}{\partial T}\right)_{P,x}\right] + x\left[\ln\gamma_2 + T\left(\frac{\partial\ln\gamma_2}{\partial T}\right)_{P,x}\right]\right\}. \tag{S16}$$

We emphasize that in all formulas relating to a mixture of gases (exact thermodynamic expressions), μ_i and γ_i mean the actual chemical potentials and volatilities. These values, generally speaking, differ from those for individual (pure) gases with the same pressure and the same temperature. However, these differences are of a higher order of smallness compared to the accuracy of the equation of state (14). Therefore, for our estimates we can safely use the fugacity coefficients of individual gases.

Values γ_1 and γ_2 can be determined from the equation of state using the well-known formula [16]

$$\ln\frac{f}{P} = \ln\gamma = \int_0^P \frac{Z(T,P)-1}{P}dP. \tag{S17}$$

The function $Z = PV_m/RT$ (compression factor) is the expression in parentheses in the virial equation (14). For a perfect gas $Z = 1$. For our real gas $Z - 1 = NB/V = nRB/V$. To use (S17), it is necessary to express Z in terms of pressure and temperature. For an accuracy corresponding to equation (14), it would be sufficient to take the ratio N/V from the equation of state of a perfect gas, and then we would put $Z - 1 = PB/T$. But for methodological purposes, we will carry out calculations with excessive accuracy, expressing $N/V = \xi$ from equation (14). To do this, you need to solve the quadratic equation

$$\xi^2 + \frac{1}{B}\xi - \frac{P}{TB} = 0 . \tag{S18}$$

The solution, which has physical meaning, is

$$\xi = \frac{1}{2B}\left(\sqrt{1+4BP/T} - 1\right). \tag{S19}$$

For a sufficiently rarefied gas, $BP/T \square 1$, and since $(1 + \varepsilon)^{1/2} \approx 1 + \tfrac{1}{2}\varepsilon$ at $\varepsilon \square 1$, expression (S19) becomes $N/V = P/T$. Thus,

$$\ln\gamma = \frac{1}{2}\int_0^P \left(\sqrt{1+4BP/T} - 1\right)\frac{dP}{P} = \sqrt{1+4BP/T} - 1 - \ln\frac{1}{2}\left(1 + \sqrt{1+4BP/T}\right). \tag{S20}$$

If we take into account that $\ln(1 + \varepsilon) \approx \varepsilon$ at $\varepsilon \square 1$, then in a more "correct" (less accurate) approximation $\ln\gamma \approx BP/T$.

To calculate the terms in (S16) containing the temperature derivative, we use the well-known relationship between the coefficient B and the van der Waals parameters a and b: $B = b + a/T$ (see Section 4 of the main text). Then we get

$$T\left(\frac{\partial \ln\gamma}{\partial T}\right)_P = -\frac{2P}{T}\frac{b+2a/T}{1 + \sqrt{1+4P(b+a/T)/T}} . \tag{S21}$$

Numerical results for neon and argon, obtained using formulas (S20), (S21) at 300 K and a pressure of 0.5 atm, are presented in Table S4.

Table S4. The fugacity coefficients of two rarefied gases, calculated with different accuracies

Gas	Quantity	Excessive precision	Adequate accuracy
Neon	$\ln\gamma_1$	0.000520662	0.000520797
	γ_1	1.000520797	1.000520933
	$T(\partial\ln\gamma_1/\partial T)_P$	−0.000694199	−0.001389120
Argon	$\ln\gamma_2$	0.001761321	0.001762871
	γ_2	1.001763873	1.001764426
	$T(\partial\ln\gamma_2/\partial T)_P$	−0.002867037	−0.005744164

Calculation using formula (S16) for an equimolar mixture of neon and argon at a total pressure of 1 atm leads to the result $S^E = 0.00531785$ J·K^{-1}. Comparison with the entropy of mixing $\Delta S = 5.29330$ J·K^{-1}, obtained without taking this correction into account, suggests that the additivity approximation is legitimate.

Section S4. Selected information about quantum gases

The name "quantum gases" implies a deviation from an ideal (Boltzmann) gas due to quantum effects. These effects are not directly related to the quantum nature of the motion of

individual particles. Indeed, translational motion remains quasi-classical, since the particles move in a macroscopic volume. Thermodynamic differences between gases are determined by restrictions imposed on the placement of identical particles in states. The prohibition for fermions to occupy a certain state by more than one particle, and vice versa, the possibility of placing any number of particles in one state for bosons, represents a specific type of interaction – an exchange effect, which ultimately follows from the symmetry properties of the wave function describing a gas of indistinguishable particles.

In conditions where gases have to be considered as quantum, particles can almost always be considered elementary, *i.e.*, those that lack internal degrees of freedom. Therefore, states should be understood as wave functions of the translational motion of a particle. It is necessary, however, to take into account the spin s of the particle, which increases the statistical weight of all states by $2s + 1$ times.

To find the Fermi and Bose distributions, it is easiest to apply the grand canonical Gibbs distribution to gas subsystems that are a set of particles in a certain quantum state (with number k). The Ω_k-potential of the subsystem, containing n_k particles, is found from the sum over the states. The energy of the subsystem is $n_k \varepsilon_k$, therefore

$$\Omega_k = -T \ln \sum_{n_k=0}^{\infty} \left(e^{\frac{\mu - \varepsilon_k}{T}} \right)^{n_k},$$
(S22)

where μ is the chemical potential of the gas. For a Fermi gas $n_k = 0, 1$, therefore

$$\Omega_k = -T \ln(1 + e^{\frac{\mu - \varepsilon_k}{T}}).$$
(S23)

From here we find the average filling numbers using the thermodynamic method ($\lambda = e^{\mu/T}$):

$$\overline{n}_k = -\left(\frac{\partial \Omega_k}{\partial \mu} \right)_{T,V} = \frac{1}{e^{(\varepsilon_k - \mu)/T} + 1}.$$
(S24)

This is the Fermi – Dirac distribution. The chemical potential μ depends on the temperature. At $T = 0$ it takes the value $\mu(0) = \varepsilon_F$, which is called the Fermi energy. If $\varepsilon_k > \varepsilon_F$, then the occupation numbers are 0. If $\varepsilon_k < \varepsilon_F$, then they become 1. The Fermi gas in this state is completely degenerate.

In the case of a Bose gas, the occupation numbers can be any. Calculating the statistical sum is elementary, since the series under the logarithm sign in (S22) is a geometric progression, the summation of which yields

$$\Omega_k = T \ln(1 - e^{\frac{\mu - \varepsilon_k}{T}}).$$
(S25)

In the same way as before, we find the average filling numbers:

$$\overline{n}_k = \frac{1}{e^{(\varepsilon_k - \mu)/T} - 1}.$$
(S26)

The resulting function is the Bose – Einstein distribution.

For a gas consisting of elementary particles or particles whose internal state does not change under given conditions, the energy of a particle is reduced to the kinetic energy of translational motion $\varepsilon = p^2/2m$, which is always quasi-classical in a volume of macroscopic dimensions. Accordingly, in the energy distribution function, the index k must be omitted, and in the formulas, we must switch from summation to integration. Let us write out all three functions:

$$f_1(\varepsilon) = \lambda e^{-\varepsilon/T} \qquad \text{Boltzmann,}$$
(S27)

$$f_2(\varepsilon) = \frac{1}{\lambda^{-1}e^{\varepsilon/T}+1} \qquad \text{Fermi} - \text{Dirac,} \tag{S28}$$

$$f_3(\varepsilon) = \frac{1}{\lambda^{-1}e^{\varepsilon/T}-1} \qquad \text{Bose} - \text{Einstein.} \tag{S29}$$

The transition from summation to integration is carried out as follows. The number of particles dN_ε in the energy interval $d\varepsilon$ is found by multiplying the distribution function by the number of states falling on the given interval:

$$dN_\varepsilon = f(\varepsilon)\cdot D(\varepsilon)d\varepsilon. \tag{S30}$$

Here $D(\varepsilon)$ is the density of states at a given energy, $D(\varepsilon)d\varepsilon$ is the total number of states in the interval $d\varepsilon$. The product $f(\varepsilon)D(\varepsilon)d\varepsilon$ is the number of occupied states. Using the quasi-classical nature of translational motion, we find the number of states in the element of the phase space $d^3p\cdot dV$ of the particle:

$$g d\tau = g\frac{d^3p\cdot dV}{(2\pi\hbar)^3}, \tag{S31}$$

where $g = 2s + 1$. Since $d^3p = 4\pi p^2 dp$, where p is the momentum, then integrating over the volume and expressing the momentum through energy, we obtain

$$D(\varepsilon)d\varepsilon = gV\frac{p^2 dp}{2\pi^2\hbar^3} = \frac{gV}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{\varepsilon}\,d\varepsilon. \tag{S32}$$

Thus, the density of states of a particle on the energy scale is

$$D(\varepsilon) = V\underbrace{\frac{g}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}}_{a}\sqrt{\varepsilon}. \tag{S33}$$

As we can see, for a monatomic ideal gas in volume V, the replacement of summation over quantum states k by integration over energy ε is carried out according to the rule

$$\sum_k (...) \quad \rightarrow \quad aV\int_0^\infty (...)\sqrt{\varepsilon}\,d\varepsilon. \tag{S34}$$

Substituting (S33) into (S30), we obtain the particle energy distribution:

$$dN_\varepsilon = aV\frac{\sqrt{\varepsilon}\,d\varepsilon}{\lambda^{-1}e^{\varepsilon/T}\pm 1}. \tag{S35}$$

The total number of particles in the gas is found by integrating (S35) over $d\varepsilon$:

$$N = \int_0^\infty dN_\varepsilon = aV\underbrace{\int_0^\infty \frac{\sqrt{\varepsilon}\,d\varepsilon}{\lambda^{-1}e^{\varepsilon/T}\pm 1}}_{I} = a\cdot V\cdot I.$$

Let us rewrite this equality as follows:

$$a\int_0^\infty \frac{\sqrt{\varepsilon}\,d\varepsilon}{\lambda^{-1}e^{\varepsilon/T}\pm 1} = \frac{N}{V}. \tag{S36}$$

The energy of the gas is obtained by integrating expression (S35) multiplied by ε:

$$U = \int_0^\infty \varepsilon \, dN_\varepsilon = aV \int_0^\infty \frac{\varepsilon^{3/2} d\varepsilon}{\underbrace{\lambda^{-1} e^{\varepsilon/T} \pm 1}_{I'}} = a \cdot V \cdot I'. \tag{S37}$$

It is impossible to calculate the energy in analytical form, since the integral contains μ as a parameter, which itself depends on temperature and volume.

Consider a Fermi gas at absolute zero temperature, when it is completely degenerate. In this case, there is an upper occupied energy level ε_F (the Fermi energy), below which all states are filled and above which they are vacant. For a fixed volume, the maximum energy ε_F is determined by the number of electrons in the gas.

The number of states with the absolute value of the particle momentum in the interval between p and $p + dp$ is equal to

$$gV \frac{p^2 dp}{2\pi^2 \hbar^3}. \tag{S38}$$

Equating the number of particles filling all states with moments from zero to p_F to the number N, we obtain

$$\frac{gV}{2\pi^2 \hbar^3} \int_0^{p_F} p^2 dp = \frac{gV p_F^3}{6\pi^2 \hbar^3} = N, \tag{S39}$$

from where we find the maximum value of the impulse

$$p_F = \left(\frac{6\pi^2}{g}\right)^{1/3} \left(\frac{N}{V}\right)^{1/3} \hbar. \tag{S40}$$

At $T = 0$, the electrons in momentum space fill a sphere of radius p_F. A sphere of this radius is called the Fermi surface. From (S40) using the formula $\varepsilon_F = p_F^2/2m$, we obtain an expression for the Fermi energy:

$$\varepsilon_F = \left(\frac{6\pi^2}{g}\right)^{2/3} \frac{\hbar^2}{2m} \left(\frac{N}{V}\right)^{2/3}. \tag{S41}$$

The total energy of the gas can be obtained by multiplying the number of states (S38) by $p^2/2m$ and integrating over all moments:

$$U_0 = V \frac{g}{4m\pi^2 \hbar^3} \int_0^{p_F} p^4 dp = \frac{gV p_F^5}{20m\pi^2 \hbar^3}. \tag{S42}$$

After substituting here (S40) we arrive at the expression

$$U_0 = \frac{3}{10} \left(\frac{6\pi^2}{g}\right)^{2/3} \frac{\hbar^2}{m} \left(\frac{N}{V}\right)^{2/3} N. \tag{S43}$$

Using the equation $PV = 2U/3$, which is valid for quantum gases, we find the gas pressure:

$$P_0 = \frac{1}{5} \left(\frac{6\pi^2}{g}\right)^{2/3} \frac{\hbar^2}{m} \left(\frac{N}{V}\right)^{5/3} = \frac{2}{5} \mu_0 \frac{N}{V} = \frac{2}{3} \frac{U_0}{V}. \tag{S44}$$

Thus, the pressure of the Fermi gas at absolute zero temperature is proportional to the particle concentration to the power of 5/3.

The chemical potential of a Fermi gas at $T = 0$ (($\mu_0 = \varepsilon_F$) is expressed by formula (S41). In the next approximation, this value begins to depend on temperature. The dependence $\mu(T)$ is determined by equation (S36), which for a Fermi gas can be rewritten as

$$\int_0^\infty \frac{D(\varepsilon)d\varepsilon}{e^{(\varepsilon-\mu)/T}+1} = N \, , \tag{S45}$$

where $D(\varepsilon) = aV\varepsilon^{1/2}$ is the density of states. The number of electrons in the gas is constant, so for the integral to have a fixed value, μ must change with temperature. The difficulty is that the exact solution cannot be written in analytical form and one has to resort to numerical calculations or successive approximations.

Resources

1. L. D. Landau and E. M. Lifshitz, *Course of Theoretical Physics, V. 5: Statistical Physics*, Pergamon, Oxford, 1980.
2. G. Jeschke, *Advanced Physical Chemistry Statistical Thermodynamics*, http://www.epr.ethz.ch.
3. M. P. Kennett, *Essential Statistical Physics*, Simon Fraser University, British Columbia, 2020, https://doi.org/10.1017/9781108691116
4. P. Atkins and J. de Paula, *Physical Chemistry*, W. H. Freeman and Company, New York, 8th edn, 2002.