Full Articles

Temperature dependence of the solubility of helium and neon in organic liquids under atmospheric pressure

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The published data on the temperature dependence of the solubility of helium and neon in 37 and 32 organic liquids, respectively, were analyzed. The distribution constants of these gases between the intrinsic phase and the intermolecular space volume (accessible for the gases) of the liquids considered are independent of the liquid structure in the temperature range from 263 to 328 K.

Key words: helium, neon, organic liquids, solubility, temperature effect.

An analysis of the literature data on the solubility of noble gases and nitrogen in *n*-alkanes and other organic liquids at 298.15 K and partial pressure of gases of 101.32 kPa showed[1] that an equilibrium state in these systems can quantitatively be described in terms of the concept according to which the characteristic parameter of the liquid is the volume of its intermolecular space ($V_{l,f}$*) accessible for diffusional migrations of guest gas particles in the liquid. The van der Waals volume of a mole of atoms (molecules) ($V_{g,W}$) and the distribution constant (K_D) between the intrinsic phase and $V_{l,f}$* are the characteristic parameters of the gas.

The interrelation of the solubility of the gas n_2 ((mole of gas) (mole of solvent)$^{-1}$) to these parameters is expressed by the equations

$$n_2 = [V_{l,m}(k^* - k)]/[(K_D c_{g,\infty})^{-1} - V_{g,W}], \quad (1)$$

$$V_{l,f}^* = V_{l,m}(k^* - k) + n_2 V_{g,W}, \quad (2)$$

where $V_{l,m}$ is the molar volume of the liquid, m^3 mol^{-1}; k is its molecular packing index equal to the ratio of the van der Waals volume of a mole of the liquid ($V_{l,W}$), calculated by a known method,[2] to $V_{l,m}$; k* is the critical value of this parameter corresponding to the condition $n_2 = 0$; $c_{g,\infty}$ is the equilibrium concentration of the gas in the intrinsic phase, mol m^{-3}.

At the concentrations of helium and neon in the intrinsic phase corresponding to a pressure of 101.32 kPa, the inequality $V_{l,m}(k^* - k) >> n_2 V_{g,W}$ is knowingly fulfilled[1] and Eq. (1) takes the form

$$n_2 = K_D c_{g,\infty} V_{l,m}(k^* - k). \quad (3)$$

In addition, the parameter n_2 is related to the Ostwald coefficient (L_{21}) through the expression

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$$n_2 = L_{21} c_{g,\infty} V_{l,m}. \quad (4)$$

Therefore,

$$K_D = L_{21}(k^* - k)^{-1}. \quad (5)$$

The data presented earlier[1] suggest that at 298.15 K the distribution constants of helium and neon between the intrinsic phase and $V_{l,f}^*$ of organic liquids of different structure are the same and equal to their values in *n*-alkanes: 0.465 and 0.69, respectively.

This makes it possible to calculate the parameter k^*, which is temperature-independent according to its physical meaning

$$k^* = k_{(298)} + L_{21(298)}/K_{D(298)}. \quad (6)$$

Then Eq. (5) can be used to calculate K_D of helium and neon in various liquids from the values of L_{21} and k as a function of temperature.

The published information on the temperature dependence of the solubility of helium and neon in 37 and 32 liquids of different structure, respectively, was analyzed in terms of this approach.

Results and Discussion

The Ostwald coefficients of helium and neon in aliphatic, naphthenic, and aromatic hydrocarbons, monoatomic alcohols, halohydrocarbons, nitrobenzene, perfluoroheptane, and perfluoromethylcyclohexane, which were taken from Refs 3—21, are listed in Tables 1 and 2 along with the parameters k of the liquids at the corresponding parameters. The van der Waals volumes of the molecules needed for their calculation and the temperature dependence of the densities of the liquids approximated by the equation

$$\rho = a - bT, \quad (7)$$

are given in Table 3. The k^* parameter (see Table 3) was calculated from Eq. (6). The methods for the calculation of K_D and $L_{21,calc}$ (see Tables 1 and 2) are described below when discussing these values.

Table 1. The Ostwald coefficients (L_{21}) and distribution constants (K_D) for helium in organic liquids (k is the molecular packing index) as a function of temperature

Liquid	T/K	k	$L_{21} \cdot 10^2$		K_D
			Experiment	Calculation	
Hexane	288.15	0.533	4.28[3]	4.37	0.45
	298.45	0.525	4.78[3]	4.75	0.46
	314.95	0.513	5.97[3]	5.31	0.52
Heptane	288.15	0.545	3.65[3]	3.81	0.46
	298.15	0.539	4.13[3]	4.09	0.48
	314.95	0.527	5.07[3]	4.65	0.52
Octane	283.23	0.558	2.80[4]	3.20	0.41
	288.15	0.555	3.17[3]	3.34	0.45
	298.15	0.548	3.52[3]	3.67	0.45
	312.92	0.539	4.22[4]	4.09	0.49
	314.75	0.538	4.44[3]	4.14	0.50
Nonane	288.15	0.563	2.70[3]	2.96	0.43
	298.15	0.557	3.28[3]	3.24	0.47
	314.95	0.546	4.07[3]	3.76	0.51
Decane	283.18	0.572	2.51[4]	2.54	0.46
	288.35	0.569	2.48[3]	2.68	0.43
	298.15	0.563	2.98[3]	2.96	0.47
	313.35	0.554	3.56[4]	3.38	0.49
	314.65	0.553	3.48[3]	3.43	0.47
Dodecane	288.15	0.578	2.09[3]	2.26	0.45
	298.15	0.573	2.40[3]	2.40	0.47
	314.55	0.564	2.87[3]	2.91	0.49
Tetradecane	288.35	0.585	1.86[3]	1.93	0.46
	298.15	0.580	2.17[3]	2.16	0.47
	314.10	0.571	2.44[3]	2.58	0.45
3-Methylheptane	288.15	0.558	3.29[3]	3.48	0.44
	298.15	0.551	3.75[3]	3.81	0.46
	314.05	0.541	4.59[3]	4.28	0.51
2,3-Dimethylhexane	288.15	0.565	3.37[3]	3.48	0.46
	298.15	0.558	3.76[3]	3.81	0.47
	314.05	0.547	4.54[3]	4.32	0.49
2,2,4-Trimethylpentane	288.15	0.547	3.97[3]	4.37	0.42
	298.15	0.541	4.58[3]	4.65	0.45
	314.95	0.530	5.33[3]	5.17	0.48
Cyclohexane	288.15	0.575	2.32[5]	2.44	0.45
	293.15	0.572	2.52[5]	2.58	0.46
	298.45	0.568	2.76[3]	2.77	0.47
	303.15	0.565	2.97[5]	2.91	0.48
	314.75	0.557	3.51[3]	3.29	0.50
Methylcyclohexane	289.15	0.568	2.72[6]	2.73	0.47
	303.15	0.559	3.25[6]	3.15	0.48
	316.25	0.550	4.10[6]	3.57	0.54
Benzene	288.15	0.601	1.75[3,5]	1.74	0.48
	291.75	0.599	1.88[7]	1.83	0.48
	293.15	0.598	1.93[5]	1.88	0.48
	298.15	0.594	2.11[3,5]	2.07	0.48
	299.15	0.593	2.08[6]	2.12	0.46
	303.15	0.590	2.22[5]	2.26	0.47
	305.15	0.589	2.32[7]	2.30	0.47
	314.95	0.582	2.69[3]	2.63	0.48

(*to be continued*)

Table 1 (*continued*)

Liquid	T/K	k	$L_{21} \cdot 10^2$		K_D
			Experiment	Calculation	
Toluene	288.15	0.599	1.89[8]	1.93	0.46
	292.15	0.596	2.09[7]	2.07	0.48
	298.15	0.592	2.24[8]	2.26	0.47
	299.35	0.592	2.32[7]	2.26	0.48
	304.15	0.589	2.55[7]	2.40	0.50
	313.15	0.583	2.77[8]	2.68	0.48
	328.15	0.573	3.52[8]	3.15	0.53
o-Xylene	283.16	0.615	1.47[9]	1.50	0.46
	298.15	0.606	1.88[9]	1.93	0.46
	313.11	0.598	2.32[9]	2.30	0.47
m-Xylene	283.18	0.604	1.60[9]	1.69	0.44
	291.35	0.599	1.97[7]	1.93	0.48
	298.17	0.595	2.02[9]	2.12	0.45
	298.95	0.595	2.29[7]	2.12	0.51
	304.75	0.592	2.44[7]	2.26	0.50
	313.15	0.588	2.58[9]	2.44	0.49
p-Xylene	288.15	0.599	1.76[9]	1.83	0.45
	298.15	0.593	2.11[9]	2.12	0.47
	313.17	0.584	2.66[9]	2.54	0.49
Perfluoroheptane	291.40	0.572	8.85[12]	9.40	0.44
	295.47	0.569	9.20[12]	9.54	0.45
	299.24	0.565	9.70[12]	9.73	0.47
	303.23	0.562	10.10[12]	9.87	0.48
Perfluoromethylcyclohexane	289.15	0.591	8.65[5]	9.17	0.44
	303.15	0.579	9.91[5]	9.73	0.48
	316.15	0.567	10.60[5]	10.30	0.48
Methanol	288.15	0.551	3.13[5]	3.15	0.47
	293.15	0.545	3.36[5]	3.43	0.46
	298.15	0.542	3.57[5]	3.57	0.47
	303.15	0.539	3.80[5]	3.71	0.48
Ethanol	278.15	0.572	2.50[10]	2.54	0.46
	288.15	0.565	2.83[5]	2.87	0.46
	289.15	0.565	2.92[10]	2.87	0.48
	293.15	0.562	3.03[5]	3.01	0.47
	299.15	0.558	3.30[10]	3.20	0.48
	303.15	0.556	3.40[9]	3.29	0.49
Isobutanol	274.05	0.583	2.16[11]	2.12	0.48
	282.91	0.578	2.55[11]	2.35	0.51
	295.85	0.571	2.63[11]	2.68	0.46
	312.76	0.562	3.06[11]	3.10	0.46
Decanol	282.64	0.607	1.64[4]	1.50	0.51
	298.11	0.598	1.93[4]	1.93	0.47
	313.49	0.589	2.30[4]	2.35	0.46
Cyclohexanol	298.15	0.625	1.10[5]	1.13	0.46
	303.15	0.623	1.18[5]	1.22	0.46
	310.15	0.620	1.35[5]	1.36	0.47
Acetone	288.15	0.537	2.98[5]	3.24	0.43
	293.15	0.534	3.32[5]	3.38	0.46
	298.15	0.530	3.61[5]	3.57	0.47
Cyclohexanone	273.15	0.596	0.98[18]	0.89	0.51
	283.15	0.590	1.20[18]	1.18	0.48
Cyclohexanone	293.15	0.585	1.44[18]	1.41	0.48
	298.15	0.582	1.56[18]	1.55	0.47
	303.15	0.579	1.59[18]	1.69	0.44
Cycloheptanone	273.15	0.611	0.96[19]	0.80	0.58
	283.15	0.606	1.14[19]	1.03	0.52
	293.15	0.603	1.35[19]	1.18	0.53
	298.15	0.598	1.47[19]	1.41	0.49
	303.15	0.595	1.56[19]	1.55	0.48
2,6-Dimethylcyclohexanone	273.15	0.606	1.38[20]	1.41	0.46
	283.15	0.601	1.65[20]	1.64	0.47
	293.15	0.595	1.92[20]	1.93	0.47
	298.15	0.593	2.05[20]	2.02	0.48
	303.15	0.590	2.18[20]	2.16	0.47
Tetrachloromethane	282.74	0.560	2.24[17]	2.35	0.45
	298.14	0.550	2.70[17]	2.82	0.45
	308.15	0.543	3.12[17]	3.15	0.47
	319.13	0.587	3.41[17]	3.43	0.46
Tetrachloroethane	291.25	0.606	2.26[7]	2.26	0.47
	297.45	0.603	2.48[7]	2.40	0.49
	304.05	0.599	2.69[7]	2.58	0.49
Chlorocyclohexane	263.15	0.614	1.02[21]	0.85	0.57
	273.15	0.608	1.21[21]	1.13	0.50
	283.15	0.602	1.44[21]	1.41	0.48
	293.15	0.596	1.68[21]	1.69	0.47
	303.15	0.590	1.96[21]	1.97	0.47
Bromocyclohexane	263.15	0.630	0.78[21]	0.52	0.71
	273.15	0.625	0.94[21]	0.75	0.59
	283.15	0.619	1.14[21]	1.03	0.52
	293.15	0.613	1.35[21]	1.32	0.48
	303.15	0.608	1.62[21]	1.55	0.49
Fluorobenzene	288.15	0.602	2.57[8]	2.54	0.44
	298.15	0.594	3.00[8]	2.91	0.46
	313.15	0.581	3.60[8]	3.52	0.48
	328.15	0.568	4.19[8]	4.14	0.48
Chlorobenzene	288.15	0.608	1.39[8]	1.36	0.48
	298.15	0.602	1.66[8]	1.64	0.47
	313.15	0.593	2.11[8]	2.07	0.48
	328.15	0.584	2.53[8]	2.49	0.48
Bromobenzene	288.15	0.636	1.00[8]	1.03	0.45
	298.15	0.631	1.27[8]	1.27	0.47
	313.15	0.622	1.68[8]	1.69	0.47
	328.15	0.614	1.94[8]	2.07	0.44
Iodobenzene	288.15	0.658	0.63[8]	0.61	0.48
	298.15	0.653	0.84[8]	0.85	0.47
	313.15	0.646	1.14[8]	1.18	0.46
	328.15	0.638	1.39[8]	1.55	0.42
Nitrobenzene	288.15	0.621	0.61[8]	0.66	0.44
	298.15	0.616	0.90[8]	0.89	0.47
	313.15	0.608	1.22[8]	1.27	0.45
	328.15	0.600	1.38[8]	1.64	0.39

Table 2. The Ostwald coefficients (L_{21}) and distribution constant (K_D) for neon in organic liquids (k is the molecular packing index) as a function of temperature

Liquid	T/K	k	$L_{21} \cdot 10^2$		K_D
			Experiment	Calculation	
Hexane	287.15	0.533	6.07[3]	6.42	0.64
	298.15	0.525	7.07[3]	6.97	0.69
	311.85	0.515	7.71[3]	7.66	0.68
Heptane	287.15	0.546	5.35[3]	5.52	0.68
	298.15	0.538	5.77[3]	6.07	0.66
	311.95	0.529	6.76[3]	6.69	0.70
Octane	287.25	0.556	4.80[3]	4.83	0.69
	298.27	0.548	5.41[3]	5.38	0.69
	298.35	0.548	5.36[3]	5.38	0.69
	312.15	0.539	6.38[3]	6.00	0.73
Nonane	287.15	0.563	4.08[3]	4.35	0.65
	298.15	0.557	4.77[3]	4.76	0.69
	312.15	0.548	5.35[3]	5.38	0.69
Decane	289.05	0.568	3.89[3]	4.00	0.66
	298.15	0.563	4.44[3]	4.35	0.69
	298.24	0.563	4.29[4]	4.35	0.67
	312.15	0.558	5.02[3]	4.69	0.73
Dodecane	289.05	0.578	2.93[3]	3.31	0.64
	298.15	0.573	3.47[3]	3.66	0.68
	312.15	0.564	3.87[3]	4.28	0.64
Tetradecane	289.05	0.585	2.82[3]	2.83	0.69
	298.15	0.580	3.16[3]	3.17	0.69
	313.25	0.572	3.62[3]	3.73	0.67
3-Methyl-heptane	287.15	0.558	5.10[3]	5.11	0.69
	298.15	0.551	5.51[3]	5.59	0.68
	312.15	0.542	6.47[3]	6.21	0.72
2,3-Dimethyl-hexan	287.15	0.566	4.85[3]	5.04	0.66
	298.15	0.558	5.56[3]	5.59	0.69
	312.15	0.548	6.25[3]	6.28	0.69
2,2,4-Trimethyl-pentane	289.30	0.547	6.25[3]	6.42	0.67
	298.15	0.541	6.82[3]	6.83	0.69
	312.15	0.532	7.54[3]	7.45	0.70
Cyclohexane	287.15	0.576	3.64[3]	3.52	0.71
	288.15	0.575	3.48[5]	3.59	0.67
	292.97	0.572	3.98[14]	3.80	0.72
	293.15	0.572	3.80[5]	3.80	0.69
	298.15	0.568	4.07[5]	4.07	0.69
	298.15	0.568	3.92[3]	4.07	0.66
	299.53	0.567	4.35[14]	4.14	0.72
	303.15	0.565	4.35[5]	4.28	0.70
	304.75	0.564	4.65[14]	4.35	0.74
	310.50	0.560	5.08[14]	4.62	0.76
	312.15	0.558	4.69[3]	4.76	0.68
Methylcyclo-hexane	289.15	0.568	3.95[6]	4.00	0.68
	303.15	0.559	4.54[6]	4.62	0.68
	316.25	0.550	5.62[6]	5.24	0.74
Perfluoromethyl-cyclohexane	289.15	0.591	13.20[6]	13.50	0.68
	303.15	0.580	14.60[6]	14.20	0.71
	316.25	0.567	15.70[6]	15.10	0.72
Benzene	283.15	0.605	2.45[5]	2.28	0.74
	287.15	0.602	2.53[3]	2.48	0.70
	291.45	0.599	2.88[7]	2.69	0.74
	293.15	0.598	2.91[5]	2.76	0.73
	298.35	0.594	2.93[3]	3.04	0.67

Liquid	T/K	k	$L_{21} \cdot 10^2$		K_D
			Experiment	Calculation	
Benzene	298.95	0.593	3.20[7]	3.10	0.71
	304.35	0.590	3.42[7]	3.31	0.71
	310.15	0.587	3.75[5]	3.52	0.74
	312.15	0.584	4.03[3]	3.73	0.75
Toluene	288.15	0.599	2.81[8]	2.83	0.68
	292.15	0.596	3.05[7]	3.04	0.69
	298.15	0.592	3.21[8]	3.31	0.67
	299.35	0.592	3.44[8]	3.31	0.72
	304.15	0.589	3.70[8]	3.52	0.72
	313.15	0.583	3.84[7]	3.93	0.67
	328.15	0.573	4.67[7]	4.62	0.70
m-Xylene	291.65	0.599	2.87[7]	2.83	0.70
	298.17	0.595	3.20[9]	3.10	0.71
	299.25	0.595	3.30[7]	3.10	0.73
	305.25	0.591	3.56[7]	3.38	0.73
Methanol	288.15	0.551	4.36[5]	4.24	0.71
	293.15	0.545	4.64[5]	4.55	0.69
	298.15	0.542	4.59[5]	4.83	0.66
	303.15	0.539	5.11[5]	5.04	0.70
	310.15	0.534	5.43[5]	5.38	0.70
Ethanol	283.15	0.568	3.99[15]	4.00	0.69
	288.15	0.565	4.02[5]	4.21	0.66
	293.15	0.562	4.32[5]	4.42	0.68
	293.15	0.562	4.30[15]	4.42	0.67
	298.15	0.559	4.55[5]	4.62	0.68
	303.15	0.556	4.74[15]	4.83	0.68
	310.15	0.552	5.03[5]	5.11	0.68
	313.15	0.550	5.45[15]	5.24	0.72
Isobutanol	274.07	0.583	3.24[11]	3.11	0.72
	283.01	0.578	3.57[11]	3.45	0.71
	298.40	0.570	4.04[11]	4.00	0.70
	312.77	0.562	4.49[11]	4.55	0.68
Cyclohexanol	298.15	0.625	1.66[9]	1.66	0.69
	303.15	0.623	1.78[5]	1.79	0.68
	310.15	0.620	1.95[5]	2.00	0.67
Acetone	288.15	0.537	4.42[5]	4.76	0.64
	293.15	0.534	4.82[5]	4.97	0.67
	298.15	0.530	5.20[5]	5.24	0.68
Cyclohexanone	273.15	0.596	1.47[18]	1.31	0.77
	283.15	0.590	1.78[18]	1.72	0.71
	293.15	0.585	2.08[18]	2.07	0.69
	298.15	0.582	2.21[18]	2.28	0.67
	303.15	0.579	2.31[18]	2.48	0.64
Cycloheptanone	273.15	0.611	1.38[19]	1.17	0.81
	283.15	0.606	1.60[19]	1.52	0.73
	293.15	0.603	1.82[19]	1.72	0.73
	298.15	0.598	1.95[19]	2.07	0.65
	303.15	0.595	2.09[19]	2.28	0.63
2,6-Dimethyl-cyclohexanone	273.15	0.606	2.07[20]	2.07	0.69
	283.15	0.601	2.39[20]	2.42	0.68
	293.15	0.595	2.70[20]	2.83	0.66
	298.15	0.593	2.86[20]	2.97	0.66
	303.15	0.590	3.02[20]	3.17	0.66

(*to be continued*)

Table 2 (*continued*)

Liquid	T/K	k	$L_{21}\cdot10^2$		K_D
			Experiment	Calculation	
Tetrachloroethane	291.45	0.606	3.16[7]	3.31	0.66
	298.85	0.602	3.47[7]	3.59	0.67
	304.95	0.599	3.80[7]	3.80	0.69
Chlorocyclohexane	263.15	0.614	1.55[21]	1.24	0.86
	273.15	0.608	1.82[21]	1.66	0.76
	283.15	0.602	2.10[21]	2.07	0.70
	293.15	0.596	2.40[21]	2.48	0.67
	303.15	0.590	2.76[21]	2.90	0.66
Bromocyclohexane	263.15	0.630	1.18[21]	0.76	1.07
	273.15	0.625	1.38[21]	1.10	0.86
	283.15	0.619	1.61[21]	1.52	0.73
	293.15	0.613	1.86[21]	1.93	0.66
	303.15	0.608	2.15[21]	2.28	0.65
Fluorobenzene	288.15	0.602	3.69[8]	3.73	0.68
	298.15	0.594	3.95[8]	4.28	0.64
	313.15	0.581	4.91[8]	5.18	0.65
	328.15	0.568	5.67[8]	6.07	0.64
Chlorobenzene	288.15	0.608	1.99[8]	2.00	0.69
	298.15	0.602	2.36[8]	2.42	0.67
	313.15	0.593	2.90[8]	3.04	0.66
	328.15	0.584	3.57[8]	3.66	0.67
Bromobenzene	288.15	0.636	1.60[8]	1.52	0.73
	298.15	0.631	1.79[8]	1.86	0.66
	313.15	0.622	2.24[8]	2.48	0.62
	328.15	0.614	2.66[8]	3.04	0.60
Iodobenzene	288.15	0.658	0.96[8]	0.90	0.74
	298.15	0.653	1.18[8]	1.24	0.66
	313.15	0.646	1.41[8]	1.72	0.56
	328.15	0.638	1.84[8]	2.28	0.56
Nitrobenzene	288.15	0.621	0.74[8]	0.97	0.53
	298.15	0.616	1.22[8]	1.31	0.64
	313.15	0.608	1.42[8]	1.86	0.53
	328.15	0.600	1.73[8]	2.42	0.49

The comparison of the van der Waals volumes of the liquids with the dimensions of helium ($V_{g,W}$ = $= 5.9\cdot10^{-6}$ m^3 mol^{-1}) and neon ($V_{g,W} = 10.3\cdot10^{-6}$ m^3 mol^{-1}) atoms shows that the inequality $V_{l,W} \geq 2.5V_{g,W}$, which is the necessary condition of independence of $V_{l,f}$* of the liquid on the atom (molecule) size of the dissolving gas,[1] is valid save for the methanol—Ne system. Therefore, it could be expected that only for methanol the difference in k* values calculated from the sorption of helium and neon will exceed the doubled inaccuracy of the calculation of this parameter (at the standard error in determination of L_{21} equal to ±2%, the error of calculation of k* by Eq. (6) is $\pm2\cdot10^{-3}$). As it turned out (see Table 3), for all other liquids this difference does not exceed the indicated value, which allows one to use the arithmetical mean of the k*(He) and k*(Ne) values in further calculations.

For n-alkanes $k^* = 0.626\pm0.002$ is well consistent with the value calculated from the solubility of all noble gases and nitrogen[1] ($k^* = 0.626\pm0.006$) in these liquids at 298.15 K. The k* values for cyclohexane, methylcyclohexane, ethanol, isobutanol, decanol, and cycloheptanol also fall on the same region. For benzene, toluene, m- and p-xylenes, 2,3-dimethylhexane, 2,2,4-trimethylpentane, chlorobenzene, and bromocyclohexane $k^* = 0.638\pm0.002$. The lowest k* value (0.606) is characteristic of acetone, and perfluoromethylcyclohexane has the highest value (0.786).

The results of calculations of K_D for helium and neon in the liquids considered by Eq. (5) are given in Tables 1 and 2, respectively.

As can be seen, for n-alkanes at 283—315 K the K_D values of helium are ranging from 0.41 to 0.52 ($\bar{K}_D$ = $= 0.47\pm0.03$), whereas K_D of neon lie in the range 0.64—0.73 ($\bar{K}_D = 0.68\pm0.02$). These constants for other liquids are given in Table 4.

The K_D values of helium tend to increase with the temperature in hexane, heptane, octane, nonane, dodecane, isoalkanes, cyclohexane, methylcyclohexane, perfluoroheptane, and acetone; the trend to decreasing temperature coefficients is observed for decanol, cyclohexanone, cycloheptanone, iodobenzene, and chloro- and bromocyclohexanes; the temperature invariability is typical of decane, tetradecane, benzene, toluene, o-, m-, and p-xylenes, methanol, ethanol, isobutanol, cyclohexanol, 2,6-dimethylcyclohexanone, tetrachloromethane, tetrachloroethane, and fluoro-, chloro-, bromo-, and nitrobenzenes.

The situation is somewhat different in the case of neon: in all liquids the constant is almost temperature-invariable, except for isobutanol, cyclohexanone, cycloheptanone, chloro- and bromocyclohexanes, and bromo- and iodobenzenes, for which the K_D value decreases with temperature.

The evident absence of a single tendency characterizing the variation of K_D for helium and neon with temperature can reasonably be interpreted as a prove for the temperature-independent character of these values in all liquids considered, whereas deviations to this or another side can be considered as a result of systematic and random inaccuracies in the experimental determination of solubilities of the gases and densities of the liquids.

Validity of this estimation was confirmed by the data presented in the Figs 1 and 2. The experimental values of the Ostwald coefficients for He and Ne in the liquids with

Table 3. The density of some liquids (see Eq. (7)), their van der Waals volumes ($V_{l,W}$), and parameter k^* as a function of temperature

Liquid	$V_{l,W} \cdot 10^6$ /m^3 mol^{-1}	k^*		a /kg m^{-3}	$b \cdot 10$ /K^{-1}	ΔT /K	Reference
		by He	by Ne				
Hexane	69.14	0.628	0.628	927.39	9.1486	273—323	22
Heptane	79.44	0.627	0.622	933.12	8.5143	273—323	22
Octane	89.74	0.624	0.627	940.16	8.1171	273—323	22
Nonane	100.04	0.627	0.626	949.21	7.9029	273—323	22
Decane	110.34	0.627	0.627	954.89	7.6771	273—323	22
Dodecane	130.94	0.624	0.623	962.78	7.3800	273—323	22
Tetradecane	151.54	0.627	0.626	970.38	7.0841	283—323	22
3-Methylheptane	89.74	0.632	0.631	945.19	8.1622	288—314	3
2,3-Dimethylhexane	89.74	0.639	0.639	987.83	9.2927	288—314	3
2,2,4-Trimethylpentane	89.80	0.639	0.640	930.00	8.1171	273—323	22
Cyclohexane	61.80	0.627	0.627	1057.17	9.5042	283—323	20
Methylcyclohexane	72.11	0.628	0.625	1025.16	8.7257	273—323	22
Toluene	63.30	0.641	0.639	1141.24	9.3588	273—323	22
o-Xylene	73.48	0.647	0.647	1126.34	8.3971	273—323	22
m-Xylene	73.48	0.639	0.642	1108.80	8.3425	273—323	22, 23
p-Xylene	73.48	0.638	0.637	1115.05	8.6653	283—323	22, 23
Benzene	53.12	0.639	0.636	1193.19	10.7240	273—323	24
Methanol	22.05	0.618	0.612	1055.12	8.9829	273—323	24
Ethanol	32.35	0.628	0.625	1063.06	8.9500	273—323	24
Isobutanol	52.95	0.628	0.628	1020.94	7.4920	298—328	23
Decanol	114.74	0.639	0.635	1055.97	7.7545	282—298	4, 23
Tetrachloroethane	63.70	0.656	0.652	2018.92	14.4500	288—298	25, 26
Cyclohexanol	66.25	0.649	0.649	1116.34	5.7500	298—310	5, 26
Acetone	39.19	0.607	0.605	1129.05	11.5418	278—328	22
Cyclohexanone	60.64	0.616	0.614	1028.02	8.9200	273—303	27
Cycloheptanone	70.74	0.630	0.626	959.50	8.5142	273—303	19
2,6-Dimethylcyclohexanone	81.04	0.637	0.634	929.00	8.3130	273—303	20
Tetrachloromethane	53.41	0.608	0.612	2160.27	19.3175	273—323	24
Chlorocyclohexane	70.74	0.632	0.632	1286.0	9.7700	263—303	21
Bromocyclohexane	74.93	0.642	0.640	1693.0	12.2200	263—303	21
Fluorobenzene	56.04	0.658	0.654	1453.03	14.5837	288—313	8
Chlorobenzene	61.55	0.638	0.636	1424.65	10.8542	293—323	23, 25
Bromobenzene	66.55	0.658	0.657	1888.85	13.4380	273—333	24
Iodobenzene	73.42	0.671	0.670	2225.13	13.7439	293—329	23, 25
Nitrobenzene	63.30	0.635	0.634	1504.20	10.2739	273-323	23
Perfluoroheptane	128.71	0.772	—	2539.18	27.9020	291—303	13
Perfluoromethylcyclohexane	114.32	0.785	0.788	2869.67	29.8395	289—316	6

Note. ΔT is the temperature interval of the a and b coefficients in Eq. (7).

$k^* = 0.626 \pm 0.002$ (see Fig. 1) and $k^* = 0.638 \pm 0.002$ (see Fig. 2) are given in the coordinates of the equation

$$L_{21} = K_D k^* - K_D k. \qquad (8)$$

It is seen that for both groups of liquids the main array of experimental L_{21} values is rather densely grouped around the straight lines that cross the abscissa in the point corresponding to the calculated k^* value. In addition, there are L_{21} values that systematically deviate from general regularities: the solubilities of He and Ne in cycloheptanone (see Fig. 1) and in bromocyclohexane (see Fig. 2). The latters, like the solubilities of He and Ne in cyclohexanone and chlorocyclohexane as a function of temperature, are well described by the straight lines in the coordinates of Eq. (8), leading to the values of the k^* and K_D parameters given in Table 5.

These data confirm that K_D of helium and neon are temperature-independent but at the same time show that the series of experiments discussed above contains a systematic error in determination of the solubility of gases and/or the density of liquids.

A similar conclusion is based on the absence of obvious reasons for which K_D of these gases in the former two liquids could be lower than in acetone and 2,6-dimethylcyclohexanone, whereas in two other liquids they are low-

Table 4. Distribution constants (K_D) of helium and neon for the groups of liquids considered

Liquid	K_D ($\bar{K}_D$)	
	He	Ne
Isoalkanes	0.42—0.51 (0.46±0.02)	0.66—0.70 (0.69±0.02)
Cyclohexane and methylcyclohexane	0.45—0.54 (0.48±0.03)	0.66—0.76 (0.70±0.03)
Benzene and its methyl derivatives	0.44—0.53 (0.48±0.02)	0.67—0.75 (0.71±0.03)
Perfluoroalkanes and perfluoronaphthenes	0.44—0.48 (0.46±0.02)	0.68—0.72 (0.70±0.02)
Alkanols and cyclohexanol	0.46—0.51 (0.48±0.02)	0.63—0.72 (0.68±0.02)
Ketones	0.43—0.53 (0.48±0.03)	0.64—0.73 (0.68±0.04)
Tetrachloromethane and tetrachloroethane	0.45—0.49 (0.47±0.02)	0.66—0.69 (0.67±0.02)
Halobenzenes	0.42—0.48 (0.45±0.03)	0.56—0.74 (0.65±0.05)
Nitrobenzene	0.39—0.47 (0.44±0.03)	0.49—0.64 (0.55±0.06)
Chloro- and bromocyclohexanes	0.47—0.71 (0.53±0.08)	0.65—1.07 (0.76±0.13)

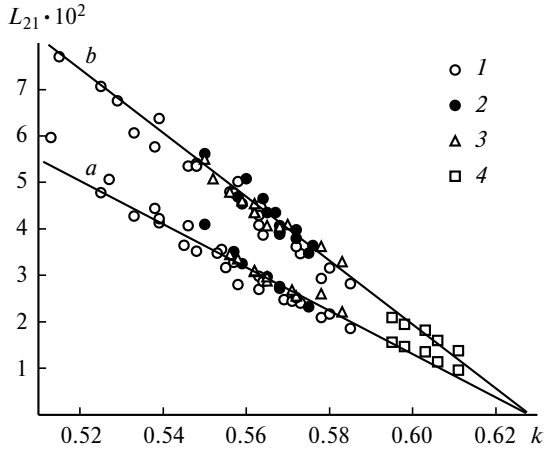

Fig. 1. The Ostwald coefficients (L_{21}) for helium (*a*) and neon (*b*) in the liquids with $k^* = 0.628 \pm 0.002$ in the coordinates of Eq. (8) as a function of temperature: *1*, *n*-alkanes; *2*, cyclohexane and methylcyclohexane; *3*, ethanol, isobutanol, and decanol; *4*, cycloheptanone.

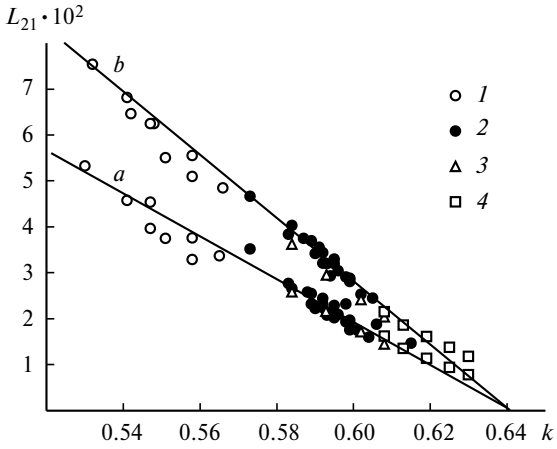

Fig. 2. The Ostwald coefficients (L_{21}) for helium (*a*) and neon (*b*) in the liquids with $k^* = 0.638 \pm 0.002$ in the coordinates of Eq. (8) as a function of temperature: *1*, isoalkanes; *2*, benzene, toluene, and *m*- and *p*-xylenes; *3*, chlorobenzene; *4*, bromocyclohexane.

er than in tetrachloromethane, tetrachloroethane, and chlorobenzene.

If the average K_D values of both gases in nitrobenzene and in chloro- and bromocyclohexane and K_D of neon in bromo- and iodobenzene are ignored, the most probable values of their distribution constants in organic liquids can be estimated as 0.47±0.01 and 0.69±0.01, respectively.

The results of calculations of the Ostwald coefficients of helium and neon in the liquids considered using the above K_D values are given in Tables 1 and 2.

A comparison of all experimental and calculated L_{21} values (without exceptions) through the parameter

$$\Delta = [(L_{21,exp} - L_{21,calc})/L_{21,exp}] \cdot 100\% \quad (9)$$

results in the distribution of deviations, indicating that the theory and experiment are in quite appropriate correspondence.

Δ	Numerical fraction	Δ	Numerical fraction
≤ ±3.0	0.482	≤ ±7.0	0.823
≤ ±4.0	0.612	≤ ±10.0	0.901
≤ ±5.0	0.694		

Thus, it can be stated that the distribution constants of He and Ne in organic liquids in the range from 263 to 328 K are temperature-independent for aliphatic, naphthenic, and aromatic hydrocarbons and alicyclic mono-

Table 5. Results of processing by Eq. (8) of the temperature dependences of the solubility of He ad Ne in some alicyclic liquids

Liquid	k^*	K_D	
		He	Ne
Cyclohexanone	0.624±0.002	0.36±0.01	0.52±0.01
Cycloheptanone	0.640±0.003	0.34±0.01	0.47±0.01
Chlorocyclohexane	0.641±0.002	0.38±0.01	0.56±0.01
Bromocyclohexane	0.654±0.003	0.33±0.01	0.47±0.01

atomic alcohols, ketones, halohydrocarbons, and perfluorinated hydrocarbons, so that they are 0.47±0.01 and 0.69±0.01, respectively. It was also shown that the temperature dependence of the gases in organic liquids reflects the change in the molar volume of the solvent and the related $V_{l,f}$* parameter rather than the thermodynamic affinity of the components of the system, as it is commonly considered.

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