TABLE I

PROPERTIES OF SOME AMINO ESTERS OF OCTANOIC, α-OCTENOIC AND α-OCTYNOIC ACIDS

Ester	B. p., °C.	Mm.	$n^{20}D$	d^{20}_4	Anal. for N Calcd.	Anal. for N Found	Time, min., for anesthesia Sensory	Time, min., for anesthesia Motor
$C_5H_{11}CH_2CH_2COOCH_2CH_2N(C_2H_5)_2$	162–164	20	1.4390	0.883	5.76	5.63	4	23.5
$C_5H_{11}CH_2CH_2COOCH_2CH_2CH_2N(C_2H_5)_2$	178–181	20	1.4405	.886	5.45	5.19	4	12.5
$C_5H_{11}CH_2CH_2COOCH_2CH_2CH_2N(C_4H_9)_2$	212–215	20	1.4451	.876	4.47	4.21	3.5	11.5
$C_5H_{11}CH{=}CHCOOCH_2CH_2N(C_2H_5)_2$	171–173	20	1.4560	.901	5.81	5.47	6.5	15
$C_5H_{11}CH{=}CHCOOCH_2CH_2CH_2N(C_2H_5)_2$	183–186	20	1.4565	.901	5.49	5.54	5	27.5
$C_5H_{11}CH{=}CHCOOCH_2CH_2CH_2N(C_4H_9)_2$	217–220	20	1.4574	.888	4.50	4.25	4	10
$C_5H_{11}C{\equiv}CCOOCH_2CH_2N(C_2H_5)_2$	150–152	7	1.4723	.916	5.86	5.81	8	24
$C_5H_{11}C{\equiv}CCOOCH_2CH_2CH_2N(C_2H_5)_2$	164–166	7	1.4739	.921	5.53	5.62	6	22
$C_5H_{11}C{\equiv}CCOOCH_2CH_2CH_2N(C_4H_9)_2$	193–195	7	1.4750	.900	4.53	4.41	4.5	10
Novocaine							8	15

ride and has the constants: b. p. 109–111° (30 mm.); $n^{20}D$ 1.4649; d^{20}_4 0.9841. *Anal.* Calcd. for $C_8H_{13}OCl$: Cl, 22.13. Found: Cl, 22.10, 22.21.

The table lists the properties and analyses of the compounds prepared and shows their relative anesthetic activity as measured by the time elapsed between contact with the drug and complete anesthesia.[4]

Some difficulty was experienced in obtaining satisfactory aqueous solutions of the compounds tested. Apparently excess acid (hydrochloric) was necessary to attain complete solution and undoubtedly this contributed to the irritating qualities noted for each compound. Novocaine is included in the table for the sake of comparison.

Summary

1. A number of amino esters of octanoic, α-octenoic, and α-octynoic acids have been prepared and their local anesthetic powers reported.

2. Within the limits of the compounds here described it appears that the anesthetic power of these amino esters is directly proportional to the molecular weight of the amino alcohol part of the molecule and inversely proportional to the degree of unsaturation of the acid.

COLUMBUS, OHIO RECEIVED AUGUST 10, 1935

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[4] The writer is indebted to Dr. T. H. Rider of the Wm. S. Merrell Company of Cincinnati for the pharmacological testing.

[CONTRIBUTION FROM THE D. I. MENDELEYEFF CHEMICAL-TECHNOLOGICAL INSTITUTE]

Thermodynamical Calculations of Solubilities of Nitrogen and Hydrogen in Water at High Pressures

BY I. R. KRICHEVSKY AND J. S. KASARNOVSKY

Much attention is given nowadays to the experimental investigation of solubilities of gases at high pressures in liquids, chiefly in water and liquid ammonia. This paper gives a method of calculation of solubilities of gases in one special, but very important, case where the solubility of gas is small and the vapor pressure of solvent is not great. The solubilities in water of such important technical gases as hydrogen, nitrogen, carbon oxide, methane, oxygen and helium fall in this classification.

When the concentration of a solute is small the fugacity of the solvent can be calculated by means of Raoult's law, the fugacities of the components being connected according to the equation of Gibbs–Duhem

$$N_1 \mathrm{d} \ln f_1 + N_2 \mathrm{d} \ln f_2 = 0 \qquad (1)$$

(N_1, N_2 and f_1, f_2 are mole fractions and fugacities of either solvent and solute); it is not difficult to prove that there exists direct proportionality between f_2 and N_2, known as Henry's law

$$f_2 = KN_2 \qquad (2)$$

where K is Henry's coefficient.

Wiebe, Gaddy and Heins[1] nevertheless have shown that their experimental data on the solubility of nitrogen in water are poorly expressed by the equation (2). This is also true for the data on the solubility of hydrogen in water. The solubilities of these gases in water are so small, even at a pressure of 1000 atmospheres, that the fugacity of water in solution can be calculated according to Raoult's law. From this, however, it would seem to follow as a thermodynamical

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[1] Wiebe, Gaddy and Heins, THIS JOURNAL, **55**, 947 (1933).

consequence that Henry's law would be obligatory for the dissolved gas. But the experimental data are evidently in contradiction to this theoretical deduction.

We shall prove that the stated contradiction occurs on account of erroneous application of the Gibbs–Duhem equation. This equation assumes that the pressure remains constant throughout the integration. In case the pressure changes but little it is possible to disregard this change as is usually done, sometimes unconsciously, when examining, for instance, the solubilities of gases at small pressures. On the contrary, when the solubilities of gases are measured at high pressures there can be no question of disregarding its influence.

It is easy to show how the usual equation of Henry has to be corrected in order to predict the solubilities of gases even at very high pressures.

When the concentration of dissolved gas changes from $N_2 = 0$ to a certain N_2, the pressure rises from $p_1°$ to P, where $p_1°$ is the vapor pressure of the pure solvent, and P is the total pressure at a concentration N_2. Agreeing that the vapor pressure of the solvent is not great, the total pressure can without any sensible error be identified with the partial pressure of gas. In order to eliminate the influence of the change of pressure on the solubility, we shall expose the solution to tension (negative pressure) which is every moment equal to $P - p_1°$. The tension must naturally affect only the solution, and not the gas phase. At such a compensation the pressure upon the solution remains constant and equal to the primary pressure $p_1°$. The integration of the Gibbs–Duhem equation becomes lawful, and supposing that the fugacity of the solvent is submitted to Raoult's law, we must obtain for the dissolved gas Henry's law

$$f_2 = KN_2' \qquad (3)$$

N_2' is, certainly, not the experimentally measured concentration of the soluted gas. N_2' is the concentration which could be obtained through compensation of the gas pressure by means of corresponding tension of the solution. K is the usual Henry's coefficient, because it is in principle determined at the zero partial pressure of gas.

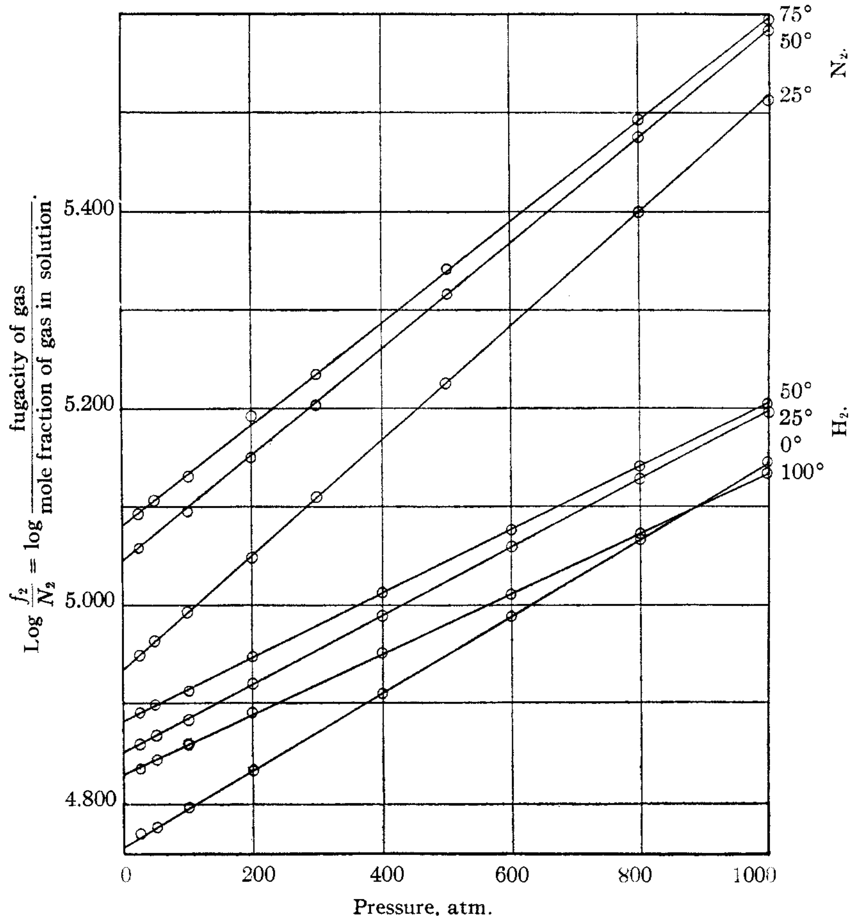

Fig. 1.

The transition from N_2' to N_2 can be made by means of the well known equation

$$\left(\frac{\partial \bar{F}_2}{\partial p}\right)_T = \bar{v}_2 \qquad (4)$$

where $\bar{F}_2$ is the partial molal free energy of the dissolved gas and $\bar{v}_2$ is its partial molal volume.

Since the concentration of gas in solution is small

$$d\bar{F}_2 = RT\, d \ln N_2 \qquad (5)$$

Substitution from equation (5) in the equation (4) gives us

$$\left(\frac{\partial \ln N_2}{\partial P}\right)_T = \frac{\bar{v}_2}{RT} \qquad (6)$$

Integration of equation (6) by the supposition of independence of $\bar{v}_2$ from pressure gives

$$\ln N_2 = \ln N_2' - \frac{\bar{v}_2 P}{RT} \qquad (7)$$

From equations (3) and (7) we receive

$$\lg \frac{f_2}{N_2} = \lg K + \frac{\bar{v}_2 P}{2.303\ RT} \qquad (8)$$

TABLE I

SOLUBILITY OF NITROGEN IN WATER

	25° $N_2 \times 10^3$		50° $N_2 \times 10^3$		75° $N_2 \times 10^3$		100° $N_2 \times 10^3$	
P, atm.	Obs.	Calcd.[a]	Obs.	Calcd.[b]	Obs.	Calcd.[c]	Obs.	Calcd.[d]
25	0.280	0.281	0.219	0.221	0.204	0.204	0.214	0.212
50	.542	.542	.436	.420	.397	.397	.415	.415
100	1.015	1.014	.8124	.8121	.760	.752	.792	.789
200	1.812	1.804	1.470	1.473	1.391	1.386	1.463	1.467
300	2.455	2.463	2.034	2.037	1.937	1.932	2.043	2.056
500	3.558	3.560	2.982	2.996	2.873	2.881	3.046	3.064
800	4.909	4.924	4.181	4.188	4.054	4.054	4.296	4.295
1000	5.720	5.710	4.900	4.879	4.750	4.736	5.006	4.981

[a] From $\lg f_2/N_2 = 4.9333 + 0.0005813\ P$. [b] From $\lg f_2/N_2 = 5.0398 + 0.0005455\ P$. [c] From $\lg f_2/N_2 = 5.0787 + 0.0005184\ P$. [d] From $\lg f_2/N_2 = 5.0608 + 0.0005130\ P$.

TABLE II

SOLUBILITY OF HYDROGEN IN WATER

	0° $N_2 \times 10^3$		25° $N_2 \times 10^3$		50° $n_2 \times 10^3$		100° $N_2 \times 10^3$	
P, atm.	Obs.	Calcd.[a]	Obs.	Calcd.[b]	Obs.	Calcd.[c]	Obs.	Calcd.[d]
25	0.4306	0.4344	0.350	0.350	0.3265	0.3263	0.3705	0.3673
50	.8635	.8631	.696	.698	.6493	.6493	.7315	.7309
100	1.709	1.703	1.386	1.380	1.293	1.289	1.448	1.449
200	3.351	3.331	2.720	2.720	2.536	2.538	2.838	2.846
400	6.390	6.395	5.250	5.250	4.929	4.935	5.466	5.507
600	9.252	9.235	7.640	7.650	7.192	7.209	7.961	7.992
800	11.91	11.87	9.910	9.918	9.337	9.359	10.32	10.31
1000	14.25	14.32	12.06	12.03	11.44	11.40	12.51	12.45

[a] From $\lg f_2/N_2 = 4.7569 + 0.0003866\ P$. [b] From $\lg f_2/N_2 = 4.851 + 0.0003465\ P$. [c] From $\lg f_2/N_2 = 4.8822 + 0.0003210\ P$. [d] From $\lg f_2/N_2 = 4.8307 + 0.0003035\ P$.

The experimental data on the solubilities of nitrogen[1] and hydrogen[2] in water agree very well with equation (8) (see Tables I and II and Fig. 1). The values of the fugacities of nitrogen and hydrogen are taken from the papers of Deming and Shupe[3] and Ångström[4] measured the increase of the volume of water due to solubility of nitrogen and hydrogen in water at 1 atmosphere.

We have calculated from his data the partial molal volumes of nitrogen and hydrogen in water solution and they are in good agreement with the values calculated from equation (8) (Table III).

For the integration of equation (6) we assumed the partial molal volume of dissolved gas to be independent of pressure, and the errors caused by this assumption appeared beyond the range of the accuracy of experimental measurements. Generally $\bar{v}_2$ is to be regarded as a function of pressure. For instance, it may be assumed to follow the simple equation

$$\bar{v}_2 = \bar{v}_2^\circ - \beta P \qquad (9)$$

where $\bar{v}_2^\circ$ is the partial molal volume at zero pressure and β is the coefficient of compressibility. Differently from pure substances β can have for the partial molal volume a negative value.[5]

TABLE III

PARTIAL MOLAL VOLUMES OF NITROGEN AND HYDROGEN IN WATER SOLUTION

	0°	25°	50°	75°	100°
			Nitrogen, cc.		
$\bar{v}_2$ obsd.	32.5				
$\bar{v}_2$ calcd.		32.8	33.4	34.1	36.2
			Hydrogen, cc.		
$\bar{v}_2$ obsd.	23.9				
$\bar{v}_2$ calcd.	20.0	19.5	19.6		21.4

In view of the accuracy of determination of the solubility of gases, it may not be very advisable

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[2] Wiebe and Gaddy, THIS JOURNAL, **56**, 76 (1934).

[3] Deming and Shupe, *Phys. Rev.*, **37**, 638 (1931); **40**, 848 (1932).

[4] Ångström, *Wied. Ann.*, **15**, 297 (1882).

[5] Adams, THIS JOURNAL, **53**, 3769 (1931); **54**, 2229 (1932).

to use equation (9) for the purpose of integrating equation (6).

It may be pointed out that our use of Raoult's law necessitates the independence of $\bar{v}_2$ from N_2.[6]

Equation (8) can also be applied to calculate the mixed solubility of slightly soluble gases, such as the solubility in water of a 3:1 mixture of hydrogen and nitrogen. In such a case in equation (8) f_2 is the fugacity of one of the gases, N_2 is its mole fraction in solution and P is total pressure. Having no experimental data about the mixed solubility of gases, we are unable to verify equation (8) by concrete examples.

Equation (8) can be used also to solve the inverse problem of calculating the fugacity of pure and mixed gases.

Summary

1. A thermodynamical equation is given which allows the calculation of the solubility of slightly soluble gases in solvents with small vapor pressure.

2. The deduced equation is verified in examples of solubilities of nitrogen and hydrogen in water at a pressure up to 1000 atmospheres and temperatures from 0 to 100°.

3. Partial molal volumes of nitrogen and hydrogen in their water solutions are calculated.

4. The possibility of calculation of the fugacity of gases on account of their solubility is shown.

MOSCOW, U. S. S. R. RECEIVED MAY 27, 1935

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[6] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 222.

[CONTRIBUTION FROM THE D. I. MENDELEYEFF CHEMICAL-TECHNOLOGICAL INSTITUTE]

Partial Molal Quantities in an Infinitely Dilute Solution

BY I. R. KRICHEVSKY AND J. S. KASARNOVSKY

The partial molal quantities g_1 and g_2 and the composition of a binary solution, expressed in mole fractions, N_1 and N_2, are connected with each other by a well-known equation, which it will be convenient for the purpose of further argumentation to set forth as follows

$$\frac{\partial \bar{g}_1}{\partial N_2}\bigg/\frac{\partial \bar{g}_2}{\partial N_2} = -\frac{N_2}{N_1} \qquad (1)$$

This equation has been submitted by Lewis and Randall for the case of an infinitely dilute solution to a special analysis. "In an infinitely dilute solution of $X_?$ in X_1, where we may write $N_2/N_1 = 0$, it is evident that either $\partial \bar{g}_1/\partial N_2$ is zero, or $\partial \bar{g}_2/\partial N_2$ is infinite. In other words, when N_2 is zero either the curve $\bar{g}_1$ becomes horizontal, or the curve of $\bar{g}_2$ becomes vertical."[1]

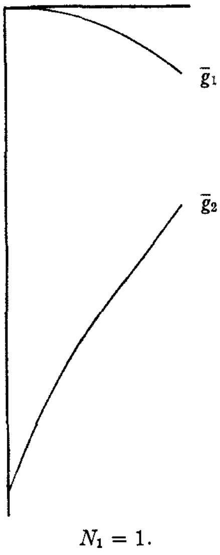

Fig. 1.

The analysis given by Lewis and Randall does not exhaust the question, inasmuch as mathematically (equation (1) is not a thermodynamical one) three other cases are possible: (1) $\partial \bar{g}_1/\partial N_2$ is zero and $\partial \bar{g}_2/\partial N_2$ is zero; (2) $\partial \bar{g}_1/\partial N_2$ is zero and $\partial \bar{g}_2/\partial N_2$ is infinite; (3) $\partial \bar{g}_1/\partial N_2$ is infinite and $\partial \bar{g}_2/\partial N_2$ is infinite.

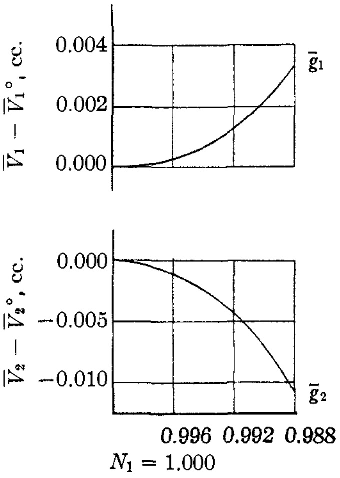

Fig. 2.—Partial molal volumes of water and ethyl alcohol at 40°.

Notwithstanding the fact that, if such allowances are made, the left part of equation (1) turns into indefiniteness, the latter at $N_2 = 0$ may have for its limit zero.

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[1] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923.