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VAN SLYKE FACTORS FOR HYDROGEN, OXYGEN,
CARBON DIOXIDE, AND CARBON MONOXIDE

by

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ABSTRACT

Tables of data calculated on an I.B.M. 610 automatic computer are given to convert the measured pressure differences in the VanSlyke gas analysis apparatus into micromolar concentration of gas in solution for hydrogen, oxygen, carbon dioxide and carbon monoxide in water. Measured solubility coefficients for carbon dioxide in various aqueous solutions of formic acid are given together with the conversion factors for use with the Van Slyke analysis apparatus.

1. Van Slyke Factors for Gases in Water

The general equation for calculating the total gas content of a solution from the amount of gas extracted in an evacuated chamber of known volume in the Van Slyke gas analysis apparatus is:⁽¹⁾

$$V_{0^{\circ}, 760} = \frac{P \times a \times i}{760 \times (1 + 0.00384 t)} \left(1 + \frac{S}{A - S} \alpha'\right) \dots \dots (1)$$

$V_{0^{\circ}, 760}$ = volume of gas in cc. at 0°C and 760 mm. pressure.

P = measured pressure difference in mm.

a = observed gas volume in cc.

i = correction factor for the reabsorption of gas in solution during the pressure measurement.

S = volume of solution in cc.

A = total volume of gas and solution during equilibration

$\alpha' = \alpha \times \frac{T}{273}$ where α is the Bunsen solubility coefficient and T is the observed temperature in °A.

t = temperature in °C. $[(1 + 0.00384 t)$ includes the correction for reading a Hg column in a glass tube.]

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To express the concentration of gas in micromoles per liter, equation (1) is modified to:

$$\mu \text{ Moles/liter} = P \left[\frac{a \times i \times 10^6}{760 \times (1 + 0.00384 t) \times 22.4} \times \frac{1}{S} \left(1 + \frac{S}{A-S} \alpha' \right) \right] \dots \quad (2)$$

or $\mu \text{ Moles/liter} = P \times F$, where F = the Van Slyke conversion factor.

This equation has been used to calculate the conversion factors for hydrogen, oxygen, carbon dioxide, and carbon monoxide in water using an I.B.M. 610 automatic computer. Values of α were taken directly from the literature,⁽²⁾ values of "i" for hydrogen, oxygen and carbon monoxide were taken as unity, while "i" for carbon dioxide was taken as 1.017.⁽¹⁾ An experimental determination of "i" for carbon dioxide in water gave a value of 1.011 ± 0.004 when the gas volume was compressed to 0.5 cc. during a time period varying from 20 to 40 seconds.

The conversion factors for hydrogen, oxygen, carbon dioxide, and carbon monoxide are summarized in Table I.

2. Measurement of the Solubility of Carbon Dioxide in Aqueous Formic Acid Solution

In the absence of any data in the literature, the solubility of carbon dioxide was determined in various aqueous solutions of formic acid ranging from pure water to pure formic acid and the solubility data used to calculate the Van Slyke conversion factors.

Aqueous solutions of formic acid were equilibrated with carbon dioxide, transferred to the Van Slyke gas analysis apparatus and the gas pressure measured at 25°C after extraction in the conventional manner. In order to eliminate the rather uncertain correction for reabsorption of gas in solution during the compression of the gas to the small measuring volume, the time to raise the mercury level was varied and the corresponding pressure recorded as a function of levelling time. The linear pressure vs. time plot was extrapolated to zero time to give a gas pressure independent of reabsorption in solution.

On completion of the last pressure measurement in the first equilibration sequence the system was again equilibrated and the gas then expelled as rapidly as possible (~ 30 sec.). The percentage of gas reabsorbed in solution during the expulsion process (see x below) could be estimated from the plot of pressure vs. levelling time determined previously. The system was now re-equilibrated and a further series of pressure measurements

Table 1

VAN SLYKE FACTORS FOR 25°C

Solvent: Water

Gas volume = 0.5 cc.

i = 1.00 H₂

Volume A = 50 cc.

i = 1.017 CO₂

Volume (S) ccs.	Factor		Volume (S) ccs.	Factor		Volume (S) ccs.	Factor	
	CO ₂	H ₂		CO ₂	H ₂		CO ₂	H ₂
5.00	5.95	5.37	8.70	3.68	3.09	14.80	2.48	1.82
5.10	5.84	5.26	8.80	3.64	3.06	15.00	2.46	1.80
5.20	5.74	5.16	8.90	3.61	3.02	15.20	2.44	1.78
5.30	5.64	5.06	9.00	3.58	2.99	15.40	2.42	1.75
5.40	5.55	4.97	9.10	3.54	2.96	15.60	2.40	1.73
5.50	5.46	4.88	9.20	3.51	2.92	15.80	2.38	1.71
5.60	5.37	4.79	9.30	3.48	2.89	16.00	2.36	1.69
5.70	5.29	4.71	9.40	3.45	2.86	16.20	2.35	1.67
5.80	5.21	4.63	9.50	3.42	2.83	16.40	2.33	1.65
5.90	5.13	4.55	9.60	3.40	2.80	16.60	2.32	1.63
6.00	5.05	4.48	9.70	3.37	2.77	16.80	2.30	1.61
6.10	4.98	4.40	9.80	3.34	2.75	17.00	2.29	1.59
6.20	4.91	4.33	9.90	3.31	2.72	17.20	2.27	1.57
6.30	4.84	4.26	10.00	3.29	2.69	17.40	2.26	1.55
6.40	4.77	4.20	10.20	3.24	2.64	17.60	2.24	1.54
6.50	4.71	4.13	10.40	3.19	2.59	17.80	2.23	1.52
6.60	4.65	4.07	10.60	3.14	2.54	18.00	2.22	1.50
6.70	4.59	4.01	10.80	3.10	2.49	18.20	2.21	1.49
6.80	4.53	3.95	11.00	3.05	2.45	18.40	2.19	1.47
6.90	4.47	3.89	11.20	3.01	2.40	18.60	2.18	1.46
7.00	4.42	3.84	11.40	2.97	2.36	18.80	2.17	1.44
7.10	4.36	3.78	11.60	2.94	2.32	19.00	2.16	1.43
7.20	4.31	3.73	11.80	2.90	2.28	19.20	2.15	1.41
7.30	4.26	3.68	12.00	2.86	2.25	19.40	2.14	1.40
7.40	4.21	3.63	12.20	2.83	2.21	19.60	2.13	1.38
7.50	4.16	3.58	12.40	2.80	2.17	19.80	2.12	1.37
7.60	4.12	3.54	12.60	2.76	2.14	20.00	2.11	1.36
7.70	4.07	3.49	12.80	2.73	2.11	20.50	2.09	1.32
7.80	4.03	3.46	13.00	2.70	2.07	21.00	2.08	1.29
7.90	3.98	3.40	13.20	2.68	2.04	21.50	2.06	1.26
8.00	3.94	3.36	13.40	2.65	2.01	22.00	2.04	1.23
8.10	3.90	3.32	13.60	2.62	1.98	22.50	2.03	1.21
8.20	3.86	3.28	13.80	2.60	1.95	23.00	2.02	1.18
8.30	3.82	3.24	14.00	2.57	1.93	23.50	2.01	1.16
8.40	3.78	3.20	14.20	2.55	1.90	24.00	2.00	1.14
8.50	3.75	3.16	14.40	2.53	1.87	24.50	2.00	1.11
8.60	3.71	3.13	14.60	2.50	1.85	25.00	1.99	1.09

Temperature Corrections /°C			
	Volume	CO ₂	H ₂
	5.00	0.036	0.019
	7.50	0.030	0.013
	10.00	0.026	0.009
	12.50	0.026	0.008
	15.00	0.026	0.006
	17.50	0.026	0.006
	20.00	0.027	0.005
	22.50	0.028	0.004
	25.00	0.030	0.004

For every °C less than 25°C add the correction

For every °C more than 25°C subtract the correction

For O₂ add 0.01 to the H₂ factors.

For CO use the H₂ factors directly.

was made. The solubility of the carbon dioxide was calculated in the following way:

Let V = total amount of gas in the original solution.

v_1 = measured volume of gas at the 1st equilibration.

v_2 = measured volume of gas at 2nd equilibration.

$$\text{1st Equilibration: } \frac{v_1}{V - v_1} = K.$$

2nd Equilibration: After expulsion of gas from the first equilibration the total amount of gas is now $V - (1 - x/100)v_1$, where x is the % of gas reabsorbed in solution during the gas expulsion. x is taken as equal to the percentage difference between the pressure measured previously for a mercury levelling time equal to the gas expulsion time and the pressure extrapolated to zero time. x varied from 1.2% for water to 5% for pure formic acid.

$$\frac{v_2}{V - (1 - x/100)v_1 - v_2} = K$$

$$\frac{v_1}{V - v_1} = \frac{v_2}{V - (1 - x/100)v_1 - v_2}$$

$$\text{therefore: } V = \frac{v_1^2 (1 - x/100)}{v_1 - v_2}.$$

Thus with V calculated from the experimental data, α , the Bunsen solubility coefficient, is readily calculated. The measured Bunsen solubility coefficients are given as a function of formic acid concentration in Figure 1.

FIGURE 1.
SOLUBILITY OF CO_2 IN AQUEOUS
FORMIC ACID SOLUTIONS.

3. Van Slyke Conversion Factors for Carbon Dioxide in Aqueous Solutions of Formic Acid

The conversion factors were calculated from equation (2) and the measured solubility coefficients using an I.B.M. 610 automatic computer. In the computations "i" factors for a mercury levelling time of 30 seconds are used and the tabulated conversion factors are applicable with negligible error for levelling times ranging from 20 to 40 seconds.

Table 2 summarizes the Van Slyke conversion factors for carbon dioxide in various aqueous formic acid solutions at 25°C. No temperature corrections are given as the carbon dioxide solubility measurements were made only at 25°C but the same percentage corrections as those for carbon dioxide in water could be used with probable negligible error.

References

1. D. O. Van Slyke and J. M. Neill, J. Biol. Chem. 61, 523 (1924).
2. "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio (1952).

Table 2

VAN SLYKE FACTORS FOR MIXTURES OF FORMIC ACID AND WATER

Temperature = 25°C

Gas volume = 0.5 cc

(For CO₂)

1-factors included

Volume A = 50 cc

Vol	5M	10M	15M	20M	26.6M	Vol	5M	10M	15M	20M	26.6M
(S)											
5.00	6 119	6 361	6 692	7 127	9 041	15.20	2 668	2 955	3 357	3 893	6 264
5.20	5 913	6 155	6 486	6 922	8 839	15.40	2 650	2 938	3 343	3 881	6 266
5.40	5 722	5 965	6 296	6 732	8 654	15.60	2 632	2 922	3 329	3 871	6 268
5.60	5 546	5 788	6 120	6 557	8 484	15.80	2 615	2 907	3 316	3 860	6 271
5.80	5 381	5 624	5 956	6 394	8 326	16.00	2 599	2 892	3 303	3 851	6 276
6.00	5 228	5 471	5 804	6 243	8 180	16.20	2 583	2 878	3 291	3 842	6 281
6.20	5 085	5 328	5 662	6 102	8 045	16.40	2 568	2 865	3 280	3 834	6 286
6.40	4 951	5 194	5 529	5 971	7 919	16.60	2 554	2 852	3 270	3 827	6 293
6.60	4 826	5 069	5 405	5 848	7 802	16.80	2 540	2 839	3 260	3 820	6 301
6.80	4 708	4 952	5 288	5 732	7 693	17.00	2 526	2 828	3 250	3 814	6 309
7.00	4 597	4 841	5 178	5 624	7 591	17.20	2 513	2 816	3 241	3 808	6 318
7.20	4 492	4 737	5 075	5 523	7 496	17.40	2 501	2 806	3 233	3 804	6 328
7.40	4 393	4 639	4 978	5 427	7 408	17.60	2 489	2 795	3 225	3 799	6 339
7.60	4 300	4 546	4 886	5 337	7 324	17.80	2 477	2 786	3 218	3 795	6 350
7.80	4 211	4 458	4 800	5 252	7 247	18.00	2 466	2 776	3 212	3 792	6 362
8.00	4 128	4 375	4 718	5 171	7 174	18.20	2 456	2 768	3 205	3 790	6 375
8.20	4 048	4 296	4 640	5 095	7 106	18.40	2 445	2 759	3 200	3 788	6 389
8.40	3 973	4 222	4 567	5 024	7 042	18.60	2 436	2 752	3 195	3 786	6 404
8.60	3 901	4 151	4 497	4 956	6 981	18.80	2 426	2 744	3 190	3 785	6 419
8.80	3 833	4 083	4 431	4 891	6 925	19.00	2 417	2 737	3 186	3 784	6 435
9.00	3 768	4 019	4 368	4 830	6 872	19.20	2 409	2 731	3 182	3 784	6 452
9.20	3 706	3 958	4 308	4 772	6 823	19.40	2 401	2 724	3 179	3 785	6 469
9.40	3 646	3 899	4 251	4 717	6 776	19.60	2 393	2 719	3 176	3 786	6 487
9.60	3 590	3 844	4 196	4 664	6 732	19.80	2 386	2 713	3 173	3 788	6 506
9.80	3 536	3 791	4 145	4 615	6 692	20.00	2 379	2 708	3 171	3 790	6 526
10.00	3 484	3 740	4 095	4 567	6 653	20.20	2 372	2 704	3 170	3 792	6 547
10.20	3 435	3 691	4 048	4 522	6 617	20.40	2 366	2 700	3 169	3 795	6 568
10.40	3 387	3 645	4 003	4 479	6 584	20.60	2 360	2 696	3 168	3 799	6 590
10.60	3 342	3 600	3 960	4 439	6 552	20.80	2 354	2 693	3 168	3 802	6 612
10.80	3 298	3 558	3 919	4 400	6 523	21.00	2 349	2 690	3 168	3 807	6 636
11.00	3 256	3 517	3 880	4 363	6 496	21.20	2 344	2 687	3 169	3 812	6 660
11.20	3 216	3 478	3 843	4 327	6 470	21.40	2 340	2 685	3 170	3 817	6 685
11.40	3 178	3 441	3 807	4 294	6 447	21.60	2 335	2 683	3 171	3 823	6 710
11.60	3 141	3 405	3 773	4 262	6 425	21.80	2 332	2 681	3 173	3 829	6 737
11.80	3 105	3 370	3 740	4 231	6 405	22.00	2 328	2 680	3 175	3 836	6 764
12.00	3 071	3 337	3 708	4 202	6 386	22.20	2 325	2 679	3 178	3 843	6 792
12.20	3 038	3 305	3 678	4 175	6 369	22.40	2 322	2 679	3 181	3 851	6 821
12.40	3 006	3 275	3 650	4 148	6 354	22.60	2 319	2 679	3 184	3 859	6 850
12.60	2 976	3 246	3 622	4 123	6 339	22.80	2 317	2 679	3 188	3 868	6 880
12.80	2 947	3 218	3 596	4 099	6 327	23.00	2 315	2 679	3 192	3 877	6 911
13.00	2 918	3 191	3 571	4 077	6 315	23.20	2 313	2 680	3 197	3 887	6 943
13.20	2 891	3 165	3 547	4 055	6 305	23.40	2 311	2 681	3 202	3 897	6 976
13.40	2 865	3 140	3 524	4 035	6 296	23.60	2 310	2 683	3 207	3 908	7 010
13.60	2 840	3 116	3 502	4 015	6 288	23.80	2 309	2 685	3 213	3 919	7 044
13.80	2 815	3 093	3 480	3 997	6 281	24.00	2 309	2 687	3 219	3 930	7 079
14.00	2 792	3 071	3 460	3 979	6 276	24.20	2 309	2 690	3 226	3 942	7 115
14.20	2 769	3 049	3 441	3 963	6 271	24.40	2 309	2 693	3 233	3 955	7 152
14.40	2 747	3 029	3 423	3 947	6 268	24.60	2 309	2 696	3 240	3 968	7 190
14.60	2 726	3 009	3 405	3 932	6 266	24.80	2 310	2 700	3 248	3 981	7 229
14.80	2 706	2 990	3 388	3 918	6 264	25.00	2 311	2 704	3 256	3 995	7 269
15.00	2 687	2 972	3 372	3 905	6 264						
	1=	1=	1=	1=	1=		1=	1=	1=	1=	1=
	1 015	1 020	1 025	1 030	1 050		1 015	1 020	1 025	1 030	1 050