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Vapor Pressures of Some α-Amino Acids

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The vapor pressures of several amino acids have been determined by the Knudsen cell effusion method. The thermodynamic quantities for the heat of sublimation, the entropy of sublimation, and the free energy of sublimation at the mean experimental temperature, 455° K., are calculated. The sensitivity of a mass spectrometer is calculated for an amino acid from its vapor pressure, its ionization cross-section, and the intensity of the (P-COOH)$^+$ ion currents relative to the total ion intensity.

A METHOD for the quantitative analysis of amino acid mixtures has been developed by Svec and Junk (*2*), based on empirically determined instrument sensitivities for these compounds. Since the vapor pressure of the individual acids is one of the factors upon which such sensitivities depend, a program was undertaken to measure the vapor pressures of a representative group of these compounds and then to compute relative sensitivities. Because these vapor pressures are low, the effusion technique was employed in which the loss of weight of a vessel of known physical dimensions which fulfill theoretical parameters was obtained by means of a quartz fiber microbalance. A cylindrical aluminum vessel was used whose inside dimensions were 0.375-inch in diameter, 0.562-inch deep. The cover was tantalum, 0.002-inch thick, pierced by a 0.013-inch circular hole. Research grade compounds were obtained from Calbiochem, Mann Research Laboratories, and Nutritional Biochemicals Corp.

The vapor pressures of 13 α-amino acids at various absolute temperatures are listed in Table I.

These vapor pressures as a function of temperature are given by

$$\log P_{\text{torr}} = -A/T + B$$

where A and B are constants whose least squares values are listed in Table II. The uncertainties cited in the table were also obtained by the least squares treatment in which a weighing factor proportional to $1/\sigma_P^2$ was applied to the data.

The enthalpy, free energy, and entropy of sublimation have been calculated from these data and are presented in Table III. These quantities for glycine are in good agreement with those published by Takagi, Chihara and Seki (*3*). No such data are found in the literature for other amino acids.

The relative mass spectrometer sensitivities for these α-amino acids were calculated from these vapor pressure data, the relative ionization cross sections computed by the method of Otvos and Stevenson (*1*), and the fraction of the

Table I. Vapor Pressure of Some α-Amino Acids[a]

Temp., ° K.	Press., (Torr) $\times 10^3$	Temp., ° K.	Press., (Torr) $\times 10^3$
Glycine		α-Amino-isobutyric Acid	
453	0.0587	439	0.078
457	0.0859	441	0.108
466	0.159	452	0.218
471	0.243	462	0.451
l-Alanine		*l*-Valine	
453	0.0759	438	0.0395
460	0.122	444	0.0682
465	0.203	448	0.103
469	0.258	452	0.150
l-α-Amino-*n*-butyric Acid		456	0.233
449	0.0972	*l*-Leucine	
452	0.1290	446	0.0440
455	0.163	452	0.0844
462	0.360	454	0.0936
dl-Norvaline		464	0.216
439	0.0404	*l*-Methionine	
446	0.0664	463	0.0384
452	0.1010	472	0.0622
461	0.1930	478	0.105
dl-Norleucine		485	0.163
435	0.0190	*l*-Phenylalanine	
449	0.0576	451	0.0252
461	0.129	457	0.0463
469	0.184	463	0.0758
Isoleucine		469	0.119
442	0.0763	*l*-Proline	
448	0.106	442	0.0675
453	0.172	448	0.107
456	0.209	451	0.171
461	0.262	457	0.210
Cycloleucine		465	0.307
443	0.0666	467	0.299
450	0.112		
456	0.166		
462	0.269		
468	0.351		

[a] Temperatures reported varied by ± 0.25° K.

Table II. Constants *A* and *B* in Vapor Pressure Equation

Acid	*A*/1000	*B*
Glycine	7.12 ± 0.02[a]	14.47 ± 0.05
l-Alanine	7.22 ± 0.05	14.81 ± 0.10
l-α-Amino-*n*-butyric acid	8.49 ± 0.04	17.86 ± 0.09
dl-Norvaline	6.27 ± 0.01	12.89 ± 0.05
dl-Norleucine	5.98 ± 0.03	12.05 ± 0.06
Isoleucine	6.27 ± 0.05	13.05 ± 0.23
Cycloleucine	6.44 ± 0.02	13.36 ± 0.06
α-Amino-isobutyric acid	6.57 ± 0.03	13.90 ± 0.03
l-Valine	8.49 ± 0.04	17.99 ± 0.08
l-Leucine	7.86 ± 0.04	16.28 ± 0.09
l-Methionine	6.53 ± 0.05	12.67 ± 0.10
l-Phenylalanine	8.04 ± 0.04	16.22 ± 0.08
l-Proline	5.04 ± 0.04	10.32 ± 0.09

[a] Standard deviations obtained from a least squares calculation, in which the weighting factor, $1/\sigma_P^2$, was applied.

Table III. Standard Thermodynamic Quantities for the Sublimation of Some α-Amino Acids at 455° K.

Acid	Δ*S*, Cal./Deg-Mole	Δ*H*, Kcal./Mole	Δ*G*, Kcal./Mole
Glycine	53.0 ± 0.2	32.6 ± 0.1	8.48 ± 0.1
l-Alanine	54.6 ± 0.5	33.0 ± 0.2	8.17 ± 0.3
l-α-Amino-*n*-butyric acid	68.6 ± 0.4	38.9 ± 0.2	7.73 ± 0.3
dl-Norvaline	45.8 ± 0.2	28.7 ± 0.1	7.87 ± 0.1
dl-Norleucine	42.0 ± 0.3	27.4 ± 0.1	8.32 ± 0.2
Isoleucine	46.5 ± 1.0	28.7 ± 0.2	7.54 ± 0.5
Cycloleucine	48.0 ± 0.3	29.5 ± 0.1	7.69 ± 0.2
α-Amino-isobutyric acid	50.4 ± 0.1	30.1 ± 0.1	7.17 ± 0.2
l-Valine	69.1 ± 0.4	38.9 ± 0.2	7.46 ± 0.3
l-Leucine	61.3 ± 0.4	36.0 ± 0.2	8.11 ± 0.3
l-Methionine	44.8 ± 0.5	29.9 ± 0.2	9.49 ± 0.3
l-Phenylalanine	61.0 ± 0.4	36.8 ± 0.2	9.04 ± 0.3
l-Proline	34.0 ± 0.4	23.1 ± 0.2	7.62 ± 0.3

Table IV. Relative Mass Spectrometer Sensitivities for Some α-Amino Acids

Acid	Calcd. From This Work	Empirically Determined (2)
Glycine	0.88	0.88
Alanine	0.88	0.87
l-α-Amino-*n*-butyric acid	0.84	0.89
Valine	0.96	0.96
Isoleucine	1.00	1.00

total fragment ion currents represented by the $(P\text{-}COOH)^+$ peak for each amino acid. These sensitivities are obtained from

$$S = \%(P\text{-}COOH)^+ \, (I.\,C.)\,(v.p.)^{1/2}$$

where *I. C.* is the ionization cross section. A comparison of the calculated values and those determined empirically are listed in Table IV. The good agreement between the calculated values and the only available empirical values indicates the utility of vapor pressure measurements in the determination of mass spectrometer sensitivities for substances of low vapor pressure.

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Ternary Systems: Water–Acetonitrile–Salts

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Phase equilibria data—binodal curves, tie lines, conjugation lines, and plait point—for the systems H_2O-CH_3CN-K_2CO_3, H_2O-CH_3CN-KF, and H_2O-CH_3CN-KBr are presented. The characteristics of these systems are correlated with the vapor pressure and solubility data.

ACETONITRILE and water form a binary azeotrope having 83.7 wt. % acetonitrile and boiling at 76.5° C. (760 mm. of Hg). During dehydration of acetonitrile, this mixture is usually formed. If the last trace of water must be removed, suitable entrainers which form a ternary azeotrope with the nitrile and water are used. Pratt (*12*) has shown the composition of the ternary azeotrope utilizing benzene and trichlorethylene. The same author mentioned the separation of water from acetonitrile by salting out but no reference is given. No data on dehydration of acetonitrile by liquid-liquid extraction is found in the literature; therefore, the authors decided to investigate the possibilities of salting out acetonitrile with different salts.