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1 October 1965

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U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

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NATIONAL BUREAU OF STANDARDS REPORT

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A SURVEY OF

THERMODYNAMIC PROPERTIES OF THE COMPOUNDS OF THE ELEMENTS CHNOPS

Mary K. Buresh, Martin L. Reilly, George T. Furukawa,
and George T. Armstrong

Heat Division, Institute for Basic Standards

Progress Report for the Period 1 July to 30 September 1965

to

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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FOREWORD

A study at the National Bureau of Standards (NBS), of which this is the fifth progress report, has been undertaken to meet the need of the National Aeronautics and Space Administration (NASA) for thermodynamic information on biologically related materials important to the space program for several reasons. Among these reasons are the necessity of inferring the maximum amount of useful chemistry of incompletely accessible environments, for which only limited information is available, the possibility of the occurrence of organic compounds naturally synthesized under primitive conditions, and the possibility of theoretically recovering part of the prebiological history of the earth.

This program is being carried out under the technical supervision of Dr. George Jacobs of NASA, and with the consultation of Dr. Harold Morowitz of the Yale University, Department of Molecular Biology and Biophysics, and Dr. C. W. Beckett of the Heat Division, Institute for Basic Standards (NBS). The contract (Contract No. R-138) was initiated 1 May 1964 and extended 29 April 1965. The program was extended by Amendment 1 for an additional year, beginning 1 July 1965. This report covers the first quarter of the extended contract.

George T. Armstrong

George T. Armstrong
Supervisory Chemist
Project Leader

Introduction

The survey of thermodynamic data on the compounds of the elements C-H-N-O-P-S which had been in progress for a year at the beginning of the quarter for which this report is written, had not yet provided a complete survey of the thermodynamic data available, and is being continued for an additional year. On September 1, a meeting for review and planning for work in this area was held at the NASA Headquarters. A brief, informal memorandum outlining the activity at the meeting is attached for information as Appendix I.

Most of the work which was carried on during the first year of the program was summarized and tabulated in NBS Reports 8521, 8591, 8641 and 8906. The current work underway in this quarter has not yet resulted in any completed new reviews. The partially completed literature reviews of the heat capacity data on several important compounds of the group of interest are outlined in the section beginning on page 2.

Literature Survey and Analysis of Low-Temperature Heat-Capacity Data on CHNOPS Compounds

Mary K. Buresh, Martin L. Reilly and George T. Furukawa

Analysis of heat-capacity data on the following substances has been in progress:

urea, cyanogen, glycylglycine, alanylglycine, leucylglycine, hippuric acid, hippurylglycine, creatine, creatine hydrate, creatinine, guanidine carbonate, hypoxanthine, xanthine, uric acid, adenine, guanine, allantoin, alloxan, and taurine.

It is expected that the analysis on most of the above substances will be completed during the next quarter.

A systematic compilation of a bibliography on heat-capacity data of ammonia, carbon dioxide, and water is being made. The literature data examined thus far are listed in the following section. The list is probably 30 percent complete.

Notations used to indicate the type of data found, experimental conditions, physical state of the substance, etc. are defined as follows:

c = crystalline phase

(C) = calculated from spectroscopic and molecular data

(cal) = calculated from calorimetric data obtained on the condensed phases, heat of vaporization, and compression, and adjusted for non-ideality of the gas

(emf) = calculated from emf measurements on chemical cells and other data

(eq) = calculated from chemical equilibrium data

g = gas phase

ℓ = liquid phase

(R) = review

(satd) = under saturation pressures corresponding to temperature T

tc = heat capacity

tc- = mean heat capacity over a broad range of temperature

tcj = heat capacity at constant volume

tck = ratio of the heat capacity, C_p/C_v

th = enthalpy (relative)

Literature Survey of Heat-Capacity, Enthalpy, and Entropy Data on Ammonia, Carbon Dioxide, and Water

Ammonia, NH_3, 17.03061

Physical State	Year Published	Type of Data and Temperature Range	Entropy at 298.15°K cal/deg-mol	References
g	1862	tc-, 293-468		[97]
c	1904	tc-, 85-170		[25]
c	1905	tc-, 85-170		[26]
c	1905	tc-, 85-170		[27]
ℓ,g	1913	th, 230-364 (7.43-761.4 lb/in^2)		[47]
g	1915	tc-, 492-878		[52]
ℓ	1916	th, 228-255 (R)		[64]
g	1916	th, 228-255 (R)		[64]
ℓ	1917	tc, 227-319		[87],[89]
ℓ	1918	tc, 227-319		[88]
ℓ,g	1920	tc, 303-398		[5]
c,ℓ	1924	tc, 25-221		[35]
ℓ (satd)	1925	tc, 240-323 (0-20 atm)		[23]
g	1925	tc, 193-288 (20-76 mm)		[40]
g	1925	tc, 240-423 (0-20 atm)		[23]
g	1925	tc, 258-423 (376-15,106 mm Hg)		[86]
g	1926	tc, 273-1273 (eq.)		[106]
g	1929	tc, 273-1200 (C)		[80]
c,ℓ,g	1932	tc, 10-298 (R)	47.2 ±1.0 (g) (R)	[62]
c,ℓ	1937	tc, 15-238	45.94(g)(cal)(C) S(g,239.68) = 44.13 (cal) S(g,239.68) = 44.10 (C)	[90]
g	1938	tc, 273-3273 (C)		[57]

NH_3 (Cont'd)

Physical State	Year Published	Type of Data and Temperature Range	Entropy at 298.15°K cal/deg-mol	References
g	1939	tc, 273-423 (C)		[53]
g	1939		46.034 (g)(C)	[118]
g	1952	tc, 298 (C)	46.01 (g)(C)	[98]
soln	1952		26.3 (aq)(eq.) (1 molal)	[98]
g	1954	tc, 273-1500 (R) th, 273-1500 (R)	46.03 (g) (R)	[66]
g	1954	tc, 300-600 (R)		[75]
g	1959	th, 300-6000 (C)	S(g,300) = 46.0629 (C)	[74]
g	1960	th, 400-2000 (C)		[63]

Carbon Dioxide, CO_2, 44.01015

Physical State	Year Published	Type of Data and Temperature Range	Entropy at 298.15°K cal/deg-mol	References
g	1862	tc-, 243-483		[97]
c	1904	tc-, 85-195		[25]
c	1905	tc-, 85-195		[26]
c	1905	tc-, 85-195		[27]
g	1909	tc, 293-373		[119]
ℓ	1913	tc-, 223-293		[56]
g	1913	tc-, 243-309 (138-824 lbs/sq.in)		[56]
g	1915	tc-, 492-878		[52]
c	1916	tc, 19-201		[32]
g	1919	tc, 195-293		[54]
g	1921	tck, 290		[91]
g	1922	tc-, 1273-2273 (C)		[125]
g	1925	tc, 291 (0.5-1 atm)		[40]
g	1925		52.19 (g)(C)(cal)	[4]
g	1925		49.55 (g)(eq)	[4]
c,ℓ	1926	th, 90-298		[72]
g	1926	tc, 300-3000 (eq)		[106]
g	1927	tc, 288-1273		[107]
c,ℓ	1928	tc, 80-320		[34]
g	1929	tc, 276-301		[13]
g	1929	tc-, 273-1273		[18]
g	1929	tc, 273-2800 (C)		[80]
g	1929	tc-, 3173 (50-150 atm)		[81]
g	1930	tc, 288-1473		[65]
g	1931	tc-, 273-1315		[19]
c,g	1932	tc, 10-298 (R)	50.0 ±2.0 (g)(R)	[62]

CO_2 (Cont'd)

Physical State	Year Published	Type of Data and Temperature Range	Entropy at 298.15°K cal/deg-mol	References
g	1932	tc, 300-1200 (C)	S(g,300)=51.19 (C)	[51]
g	1932	tc-, 690-871 (5.8-8.6 atm)		[36]
g	1932		51.07(g) (C)	[6]
g	1933		51.09(g) (C)	[48]
c	1934	th, 300-3500 (C) tc, 300-3500 (C)		[60]
g	1935	tc, 273-3273 (C)		[58]
g	1936	tck, 273-1273 (C) tcj, 273-1273 (C)		[105]
c	1937	tc, 16-190	51.11(g) (cal)(C) S(g,194.67) = 47.59 (cal) S(g,194.67) = 47.55 (C)	[43]
g	1937	tcj, 298-398 (amagat density 1-600)		[78]
g	1938	tc, 273-3273 (C)		[57]
g	1945	th, 298-3500 (C) tc, 298-3500 (C)	51.061(g) (C)	[124]
g	1950	th, 500-5000 (C) tc, 500-5000 (C)	S°(g,500)=56.113 (C)	[59]
g	1952	tc, 243-363 (0.5-1.5 atm)		[76]
g	1952	tc, 298 (C)	51.061(g) (C)	[98]
soln	1952		29.0(aq)(eq) (1 molal)	[98]
g	1954	tc, 50-5000 (C)	S°(g,300)=51.1066 (C)	[126]
g	1954	tc, 250-1500 (R)		[75]
g	1955	tc, 200-1500 (C) (0.01-100 atm) th, 200-1500 (C) (0.01-100 atm)	S(g,300)=51.102 (C)	[55]
g	1959	th, 300-6000 (C)	S(g,300)=51.1225 (C)	[74]

CO_2 (Cont'd)

Physical State	Year Published	Type of Data and Temperature Range	Entropy at 298.15°K cal/deg-mol	References
g	1959	th, 423-923 (R) (0-200 atm)		[71]
g	1960	th, 291-322 (1050-1200 p.s.i.a)		[68]
g	1960	th, 298 (R)	51.10(g) (R)	[21]
g	1960	th, 400-5000 (C)		[63]
g	1962	th, 313-1273 (C) (1-1400 bars)	S(g,313)=51.488 (C) (1 bar)	[101]

Water, H_2O, 18.01534

Physical State	Year Published	Type of Data and Temperature Range	Entropy at 298.15°K cal/deg-mol	References
c	1845	single value no temp. range		[24]
g	1862	tc-, 283-489		[97]
c	1864	tc-, 195-273 (R)		[67]
ℓ	1871	tc, 373		[16]
ℓ	1900	tc, 278-368		[7]
ℓ	1902	tc-, 268-293		[9]
ℓ	1902	tc, 278-368		[8]
c	1904	tc-, 21-291		[25]
c	1905	tc-, 21-255		[26]
c	1905	tc-, 21-255		[27]
c	1911	tc, 83-266		[79]
ℓ	1911	tc, 273-353		[15]
c	1913	tc, 22-87		[92]
c	1915	tc-, 227-273		[30]
ℓ	1915	tc, 272-311		[28]
ℓ	1917	tc-, 286-328		[14]
ℓ (tap water)	1917	tc-, 286-327		[14]
g	1922	tc-, 1273-2273 (C)		[125]
c	1925	th, 90-290		[73]
g	1927	tc, 373-1273 (C)		[107]
ℓ	1928		15.92 ±0.02(ℓ) (R)	[69]
g	1929	tc, 273-2800 (C)		[80]
g	1929	tc-, 289-3000 (C) (50-150 atm)		[81]
c	1930	tc, 195-270		[10]
c,ℓ	1930	tc, 195-298		[11]
ℓ (satd)	1930	th, 273-543		[82]
g (satd)	1930	th, 273-543		[82]

H_2O (Cont'd)

Physical State	Year Published	Type of Data and Temperature Range	Entropy at 298.15°K cal/deg-mol	References
c,ℓ	1932	tc, 10-298 (R)	15.9 ±0.1(ℓ) (R)	[62]
ℓ	1932		19.21(ℓ) (C)	[51]
g	1932	tc, 400-1200 (C)	S(g,1 atm,400) = 50.03 (C)	[51]
g(satd)	1932		S(g,satd,300) = 54.39 (C)	[51]
g	1933		45.26(g)(cal)	[42]
g	1933		45.17(g) (C)	[42]
g	1933		45.19(g) (emf)	[42]
g	1933		45.1(g) (eq)	[42]
g	1933		47.93(g) (C) (with nuclear spin)	[48]
g	1934	tc, 298-1500 (C)	45.101(g) (C)	[49]
g	1934	tc, 1500-3000 (C)	S(g,1500)=59.78 (C)	[50]
g	1935	tc, 273-3273 (C)		[58]
c	1936	tc, 16-268	44.28 ±0.05(g)(cal) (without residual entropy)	[44]
ℓ(satd)	1937	th, 373-747 (56-225 kg/cm^2)		[83]
g(satd)	1937	th, 373-747 (56-225 kg/cm^2)		[83]
g	1937		45.10(g) (C)	[41]
ℓ	1938	tc, 273-373 (R)		[99]
g	1938	tc, 273-3273 (C)		[57]
ℓ(satd)	1939	tc, 273-373		[84]
ℓ(satd)	1939	th, 273-373 (C)		[84]
ℓ(satd)	1939	th, 273-647 (R)		[85]
g(satd)	1939	th, 273-647 (R)		[85]
ℓ	1940	tc, 290-321		[20]
c	1941	tc, 6-10		[29]
c	1945	tc, 5.65-9.97		[31]

H_2O (Cont'd)

Physical State	Year Published	Type of Data and Temperature Range	Entropy at 298.15°K cal/deg-mol	References
g	1945	tc, 298-3000 (C) th, 298-3000 (C)	45.106(g) (C)	[124]
ℓ	1949	tc, 273-373 (R)		[33]
ℓ	1949	tc, 313-343		[70]
g	1950	tc, 500-5000 (C) th, 500-5000 (C)	S°(g,500) = 49.344 (C)	[59]
ℓ	1952	tc, 298 (R)	16.716(ℓ) (R)	[98]
g	1952	tc, 298 (C)	45.106(g) (C)	[98]
g	1952	tc, 362-487 (92-760 mm)		[77]
ℓ	1953	tc, 273-373 (R) th, 273-373 (R)		[46]
g	1953	tc, 373 (C)		[12]
g	1954	tc, 50-5000 (C)	S(g,300)=45.137 (C)	[38]
g	1954	tc, 400-3000 (R)		[75]
g	1955	tc, 50-1150 (C) (1-100 atm) th, 50-1150 (C) (1-100 atm)	S(g,300)=45.154 (C)	[55]
ℓ,g	1957	tc, 507-655		[2]
ℓ,g	1957	tc, 556-959 (300-500 kg/cm^2)		[94]
ℓ,g	1958	tc, 507-655		[1]
ℓ,g	1958	tc, 556-959 (300-500 kg/cm^2)		[93]
ℓ,g	1958	tc, 556-959 (300-500 kg/cm^2)		[95]
ℓ,g	1958	tc, 556-959 (300-500 kg/cm^2)		[96]
ℓ,g	1958	tc, 557-972 (550-700 kg/cm^2)		[122]
g	1958	tc, 50-5000 (C)		[108]
g(satd)	1958	tc, 443-643 (R) (8.076-214.68 kg/cm^2)		[102]

H_2O (Cont'd)

Physical State	Year Published	Type of Data and Temperature Range	Entropy at 298.15°K cal/deg-mol	References
g	1958	th, 473-1273 (R) (100-1000 atm)		[100]
g	1958	tc, 573-873 (20-500 kg/cm^2)		[61]
g	1958	tc, 587-827		[109]
g	1958	th, 720-823 (199.5-404.5 kg/cm^2)		[123]
c	1959	tc, 10-270 (R)	S(c,270)=8.99 (R)	[45]
ℓ	1959	tc, 273-519 (R)		[39]
ℓ	1959	tc, 293-573 (50-500 kg/cm^2)		[111]
ℓ,g	1959	tc, 285-774 (26-500 kg/cm^2)		[112]
g	1959	th, 300-6000 (C)	S(g,300)=45.1159 (C)	[74]
g	1959	tc, 373-923 (R) (1-700 kg/cm^2)		[103]
soln (sea water)	1959	tc, 275-304 (0-39.786 g/kg salinity)		[22]
c	1960	tc, 2-27		[37]
ℓ	1960	th, 350-373 (R)		[63]
ℓ,g (satd)	1960	tc, 273-613 (R) (0.006228-148.96 kg/cm^2)		[104]
ℓ,g	1960	tc, 273-613 (C)		[120]
ℓ,g	1960	tc, 285-774 (26-500 kg/cm^2)		[117]
g	1960	th, 298 (R)	45.11(g) (R)	[21]
g	1960	th, 400-5000 (C)		[63]
g	1960	th, 473-873 (5-225 kg/cm^2)		[17]
g	1960	tc, 613-773 (R) (293-500 kg/cm^2)		[116]
g	1960	tc, 736-872 (300-500 kg/cm^2)		[113]

H_2O (Cont'd)

Physical State	Year Published	Type of Data and Temperature Range	Entropy at 298.15°K cal/deg-mol	References
ℓ,g	1961	tc, 333-1273 (R) (0-1000 kg/cm^2)		[121]
ℓ,g	1962	tc, 323-725		[3]
ℓ,g	1962	tc, 578-775 (125-275 kg/cm^2)		[114]
g	1962	tc, 620-869 (60-225 kg/cm^2)		[115]
ℓ(satd)	1963	tc, 273-645 (0.006-215.63 x 10^5 n/m^2)		[110]
g(satd)	1963	tc, 273-645 (0.006-215.63 x 10^5 n/m^2)		[110]

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FORM CD-121 (9-22-59)
(PRES. BY A.O. 206-10)

APPENDIX I

UNITED STATES GOVERNMENT

Memorandum

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

TO : Project 221-0429 Files

DATE: September 2, 1965

FROM : G. T. Armstrong

SUBJECT: Meeting on CHNOPS program progress
at NASA Headquarters,
September 1, 1965

Present at the meeting were

Prof. H. A. Morowitz - Yale University, presiding
Dr. Goel - Yale University and University of Maryland
Drs. C. W. Beckett, G. T. Armstrong and G. T. Furukawa, NBS
Drs. M. O. Dayhoff, R. V. Eck, and one other from
National Biomedical Research Foundation
Prof. E. R. Lippincott - University of Maryland
Dr. Freeman Quimby - NASA

The meeting consisted of presentations by each of the groups present in which they discussed to a greater or less extent tasks performed, present status, difficult problems, and modes of action in the future.

Armstrong and Furukawa started with a description of the work at the NBS on the literature search and evaluation of thermodynamic data.

Margaret Dayhoff for NBRF described calculations of equilibrium compositions which were plotted on a CHO triangle.

Richard Eck described calculations of planetary atmospheres, in which the atmosphere of the Earth and Jupiter are shown to be not at equilibrium. The data for the compositions of the atmospheres of Venus and Mars are inadequate for definitive statements, but no information available is inconsistent with equilibrium atmospheres.

Ellis Lippincott described an experimental study of electrode discharge processes in atmospheres selected from the NBRF charts in which the formation of aromatic hydrocarbons (asphalt line) was confirmed.

Harold Morowitz proposed phospholipids (phosphate-fatty acid mixed esters of glycerol) as an important group of ubiquitous compounds. They are ubiquitous ingredients of the cell membrane, forming a layer ~40A° thick bounded by a layer of protein on each side. The primitive character of these lipids is inferred by Morowitz from the fact that they are non-specific with respect to fatty acids. (Various fatty acids can be substituted at random.)

Harold Morowitz presented a picture of non-equilibrium and the formation of excessive amounts of higher-than-equilibrium quantities of complex compounds as a natural consequence of the fact that the earth lies as an intermediate between an energy source (the sun) and an energy sink (outer space).

The meeting was brought to a close (4:00 P.M.) by a discussion of the selection of type compounds of several categories for attempts to get as much thermodynamic information as possible, with a view that other compounds of the same categories would not offer essentially new information.

Compounds suggested were

Glycine (heat of sol'n, vap'n)	Glycerol
Thioacetic acid	Phosphoserine
H_2S	Fatty acids
Phosphites and phosphates (vs. pH)	
D ribose	
Glucose	

This list is apparently not complete. The list of ubiquitous compounds should be examined for other types.

At various points in the meeting the following thoughts were brought up:

(1) NBRF suggested that thermodynamic information be made available on tab cards or tape.

(2) Ways of estimating free energies of formation, their variation with temperature and heats of vaporization and solution would be a help to NBRF for compounds lacking data.

(3) Because the flow of energy produces some highly unstable or reactive compounds, a treatment involving an atmosphere containing small amounts of such compounds might be fruitful.