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Heat capacities of amino acids, peptides and proteins

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Abstract

The heat capacity is one of the fundamental parameters describing thermodynamic properties of a system. It has wide applications in a number of areas such as polymer chemistry, protein folding and DNA stability. To aid the scientific community in the analysis of such data, I have compiled a database on the experimentally measured heat capacities of amino acids, polyamino acids, peptides, and proteins in solid state and in aqueous solutions.

Keywords: Heat capacity; Solid state; Aqueous solutions; Amino acids; Thermodynamic properties

1. Introduction

There is an increasing interest in understanding heat capacity, the fundamental thermodynamic parameter of biologically important molecules including amino acids, peptides and proteins. Heat capacity measurements of free amino acids date back to the end of the 19th century [1,2] and the beginning of the 20th century (e.g., Refs. [3–6]). These experiments were done either in aneroid calorimeters using the Nernst method for solid amino acids [3,4] or home built solution calorimeters with the operating volume of 500 (!) ml [5]. Values for the partial molar heat capacities of three amino acids (glycine, alanine, valine) in water obtained by the latter technique are within 15% of the values obtained using modern calorimeters. However, the absolute heat capacities of several amino acids in the solid state obtained in 1935 are within an astonishing 0.6% of the values remeasured several decades later (Fig. 1). Another leap in the heat capacity measurements of biomolecules started in the 1960s when technological developments allowed the building of instruments able to measure absolute heat capacities of small quantities of these costly molecules. In the past 4 decades, several groups around the world have been pursuing this exciting area of biophysical chemistry. This vast body of experimental data on the heat capacity of amino acids, peptides and proteins has never been systematically arranged in a single database, although some undertakings towards this have been made [8,9].

In this paper I made an attempt to bring together part of this 40-year effort and compile available data

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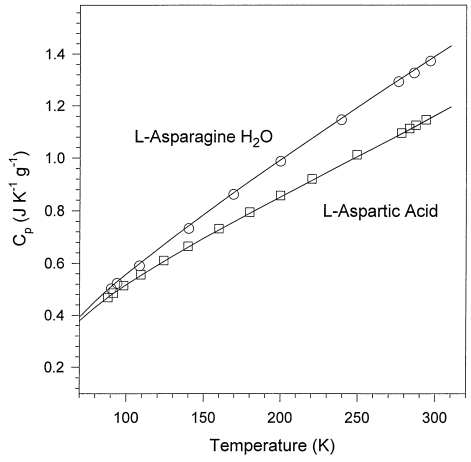

Fig. 1. Temperature dependence of the specific heat capacity of L-Asparagine H_2O (○) and L-Aspartic acid (□). Measurements performed in 1963 [7] are shown by solid lines and measurements done in 1932 [3] are given by symbols.

of the heat capacities of amino acids, peptides, and proteins. I am almost sure that some of the data has slipped by my attention, and I would like to apologize for it in advance. I would also appreciate any help in its update.

2. Definition

The heat capacity at a constant pressure, C_P, can be defined (e.g., Ref. [10]) as a temperature derivative of one of the basic thermodynamic parameters describing the state of a macroscopic system, the enthalpy, $H(T)_P$:

$$C_P = \frac{\mathrm{d}H(T)_P}{\mathrm{d}T} \tag{1}$$

Experimentally, the specific heat capacity, c_P, is equal to the heat energy, ΔQ, required to raise the unit mass of the substance by 1 K. According to the IUPAC recommendations, the specific heat capacity is measured in joules per kelvin gram ($J\ K^{-1}\ g^{-1}$). It is related to the non-SI heat capacity unit cal K^{-1} g^{-1} as 1 cal K^{-1} g^{-1} = 4.184 J K^{-1} g^{-1}.

The molar heat capacity, C_P, is obtained from the product of the molar mass, M, and the specific heat capacity:

$$C_P = M \cdot c_P \tag{2}$$

The SI unit of the molar heat capacity is J K^{-1} mol^{-1}.

The heat capacity of a system, $C_P(T)$, defined for some temperature range $(T_0–T)$ determines not only the enthalpy function of the system

$$H(T) = H(T_0) + \int_{T_0}^{T} C_P(T) \cdot \mathrm{d}T \tag{3}$$

but also its entropy, $S(T)$,

$$S(T) = S(T_0) + \int_{T_0}^{T} C_p(T) \cdot \mathrm{d}\ln T \tag{4}$$

and, thus, the Gibbs energy, $G(T)$, as well

$$G(T) = H(T) - T \cdot S(T) \tag{5}$$

Consequently, the larger the temperature range in which the $C_P(T)$ function is defined, the more complete the description of the system will be.

The total heat capacity, C_P, of a solution at constant pressure, P, may be defined in terms of the apparent heat capacity, $C_{P,\phi}$, and the concentration, w, of each of the N components:

$$C_P = \sum_{i=1}^{N} C_{P,\phi_i} \cdot w_i \tag{6}$$

The apparent heat capacity of the ith component, C_{P,ϕ_i}, is defined as a change in the total heat capacity per unit mass upon the addition of a finite amount of component i at a constant T and constant concentrations of all other components w_i:

$$C_{P,\phi_i} = \left(\frac{\partial C_P}{\partial w_i}\right)_{T,P,w_j} \quad (i \neq j) \tag{7}$$

This can be achieved by measuring the heat capacities of a series of solutions in which only the concentration of the ith component is varied. Both the heat capacities of solutions and the heat capacity of the solvent per se are plotted vs. w_i. Then, the slope of the straight line between the heat capacities of the solvent$C_{P,s}$ and the solution C_P corresponds to the apparent heat capacity of the ith component.

Table 1
Heat capacities (J K^{-1} mol^{-1}) of solid amino acids

T/K	C_P	T/K	C_P	T/K	C_P
L-Alanine (89.1 Da) [18]					
10	0.494	90	47.87	220	96.23
15	1.674	100	52.55	230	99.58
20	3.849	110	56.94	240	102.93
25	6.724	120	61.09	250	106.32
30	10.09	130	65.10	260	111.55
35	13.75	140	68.99	270	113.05
40	17.37	150	72.72	280	116.40
45	20.91	160	76.32	290	119.66
50	24.40	170	79.83	300	122.84
55	27.78	180	83.22	310	125.98
60	31.02	190	86.53	273.15	114.10
70	37.03	200	89.79	298.15	122.26
80	42.64	210	93.01	310.15	126.02
L-Arginine·HCl (210.7 Da) [19]					
10	2.326	90	105.52	220	205.10
15	6.481	100	114.68	230	212.21
20	12.25	110	123.26	240	219.37
25	19.21	120	131.46	250	226.52
30	26.91	130	139.37	260	233.72
35	34.91	140	147.15	270	241.00
40	42.93	150	154.72	280	248.20
45	50.71	160	162.09	290	255.27
50	58.16	170	169.41	300	262.25
55	65.27	180	176.65	310	269.16
60	72.05	190	183.76	273.15	243.26
70	84.43	200	190.87	298.15	260.96
80	95.48	210	197.90	310.15	269.28
L-Aspartic Acid (134.1 Da) [7]					
10	0.732	90	64.02	220	122.51
15	2.686	100	69.45	230	126.69
20	6.033	110	74.64	240	130.88
25	10.31	120	79.54	250	134.98
30	15.14	130	84.27	260	139.03
35	20.09	140	88.83	270	143.14
40	25.18	150	93.26	280	147.32
45	30.06	160	97.57	290	151.63
50	34.70	170	101.80	300	155.98
55	39.10	180	106.06	310	160.37
60	43.30	190	110.21	273.15	144.47
70	50.88	200	114.31	298.15	155.19
80	57.70	210	118.41	310.15	160.42
L-Asparagine·H_2O (150.1 Da) [7]					
10	0.686	90	76.48	220	161.21
15	2.343	100	83.93	230	167.28
20	5.376	110	91.13	240	173.34
25	9.531	120	98.07	250	179.41
30	14.63	130	104.85	260	185.44
35	20.29	140	111.46	270	191.38
40	26.18	150	117.95	280	197.28
45	32.13	160	124.35	290	203.18

Table 1 (continued)

T/K	C_P	T/K	C_P	T/K	C_P
50	37.95	170	130.71	300	208.99
55	43.56	180	136.94	310	214.81
60	48.95	190	143.09	273.15	193.26
70	58.99	200	149.12	298.15	207.90
80	68.12	210	155.19	310.15	214.89
L-Cystine (240.3 Da) [20]					
10	1.644	90	102.13	220	206.98
15	5.284	100	111.13	230	214.18
20	15.25	110	120.00	240	221.33
25	18.03	120	128.66	250	228.49
30	25.49	130	137.24	260	235.60
35	33.14	140	145.52	270	242.59
40	40.63	150	153.64	280	249.53
45	47.87	160	161.59	290	256.40
50	54.85	170	169.54	300	263.17
55	61.51	180	177.23	310	269.91
60	67.91	190	184.81	273.15	244.81
70	79.87	200	192.30	298.15	261.92
80	91.21	210	199.70	310.15	269.99
L-Glutamic Acid (147.1 Da) [7]					
10	0.276	90	70.17	220	137.24
15	2.782	100	76.53	230	142.01
20	6.259	110	82.34	240	146.78
25	10.86	120	87.95	250	151.54
30	16.12	130	93.22	260	156.31
35	21.69	140	98.37	270	161.17
40	27.18	150	103.39	280	166.11
45	32.59	160	108.41	290	171.08
50	37.80	170	113.39	300	175.98
55	42.68	180	118.24	310	180.79
60	47.28	190	122.93	273.15	162.72
70	55.65	200	127.70	298.15	175.06
80	63.18	210	132.47	310.15	180.87
L-Glutamine (146.2 Da) [7]					
10	0.728	90	72.55	220	144.06
15	2.460	100	78.99	230	149.45
20	5.791	110	84.94	240	154.72
25	10.48	120	90.67	250	159.91
30	15.91	130	196.23	260	165.02
35	21.80	140	101.76	270	170.04
40	27.72	150	107.28	280	175.10
45	33.46	160	112.63	290	180.12
50	38.93	170	117.95	300	185.10
55	44.06	180	123.18	310	189.83
60	48.87	190	128.37	273.15	171.63
70	57.66	200	133.60	298.15	184.18
80	65.48	210	138.74	310.15	189.91
Glycine (75.1 Da) [18]					
10	0.255	90	39.53	220	77.49
15	0.967	100	43.26	230	80.08
20	2.393	110	46.69	240	82.84

Table 1 (continued)

T/K	C_P	T/K	C_P	T/K	C_P
25	4.464	120	50.00	250	85.60
30	7.037	130	53.09	260	88.45
35	9.933	140	56.07	270	91.25
40	13.00	150	58.91	280	94.06
45	16.12	160	61.67	290	96.90
50	19.25	170	64.39	300	99.75
55	22.26	180	67.03	310	102.63
60	25.15	190	69.66	273.15	92.13
70	30.49	200	72.30	298.15	99.20
80	35.26	210	74.89	310.15	102.68
Glycylglycine (132.1 Da) [21]					
10	0.707	90	67.86	220	130.12
15	2.607	100	73.85	230	134.35
20	6.071	110	79.50	240	138.62
25	10.70	120	84.89	250	142.84
30	15.87	130	89.87	260	147.19
35	21.23	140	94.81	270	151.50
40	26.56	150	99.58	280	155.85
45	31.65	160	104.27	290	160.29
50	36.58	170	108.74	300	164.81
55	41.21	180	113.09	310	169.45
60	45.61	190	117.40	273.15	152.88
70	53.81	200	121.71	298.15	163.97
80	61.21	210	125.90	310.15	169.54
L-Histidine·HCl (191.6 Da) [19]					
10	1.711	90	102.63	220	195.39
15	5.690	100	111.09	230	202.13
20	11.93	110	119.04	240	208.91
25	19.33	120	126.57	250	215.81
30	27.29	130	133.85	260	222.80
35	35.38	140	140.96	270	229.87
40	43.26	150	147.90	280	236.90
45	50.88	160	154.81	290	243.89
50	58.12	170	161.63	300	250.79
55	64.81	180	168.36	310	257.65
60	71.17	190	175.14	273.15	232.09
70	82.80	200	181.92	298.15	249.53
80	93.22	210	188.66	310.15	257.73

The limiting value at $w_i \rightarrow 0$ is usually taken as a partial heat capacity, C^0_{P,ϕ_i}, of component i:

$$C^0_{P,\phi_i} = \lim_{w_i \rightarrow 0} C_{P,\phi_i} = \lim_{w_i \rightarrow 0} \left(\frac{\partial C_P}{\partial w_i} \right)_{T,P,w_j} \quad (8)$$

Consequently, the apparent heat capacity at a

Table 2
Heat capacities (J K^{-1} mol^{-1}) of solid amino acids

T/K	C_P	T/K	C_P	T/K	C_P
L-Isoleucine (131.2 Da) [22]					
10	2.741	90	74.89	220	147.53
15	6.343	100	81.80	230	152.59
20	10.80	110	88.41	240	157.74
25	15.82	120	94.68	250	162.97
30	20.93	130	100.63	260	168.16
35	26.12	140	106.36	270	173.26
40	31.22	150	111.88	280	178.53
45	36.22	160	117.24	290	183.76
50	41.08	170	122.55	300	189.28
55	45.82	180	127.70	310	194.89
60	50.38	190	132.72	273.15	174.93
70	58.95	200	137.65	298.15	188.28
80	67.15	210	142.59	310.15	194.97
L-Leucine (131.2 Da) [22]					
10	2.452	90	75.44	220	148.91
15	6.468	100	82.22	230	154.60
20	11.50	110	88.53	240	160.46
25	16.93	120	94.64	250	166.52
30	22.53	130	100.50	260	172.93
35	28.08	140	106.15	270	179.70
40	33.32	150	111.63	280	186.77
45	38.40	160	117.03	290	194.31
50	43.26	170	122.38	300	202.51
55	47.82	180	127.70	310	211.38
60	52.17	190	132.93	273.15	181.88
70	60.42	200	138.11	298.15	200.96
80	68.20	210	143.43	310.15	211.50
L-Lysine·HCl (182.7 Da) [19]					
10	2.460	90	97.74	220	186.61
15	6.594	100	106.36	230	192.92
20	12.23	110	114.47	240	199.33
25	18.82	120	122.22	250	205.81
30	25.89	130	129.54	260	212.42
35	33.08	140	136.40	270	219.16
40	40.11	150	143.05	280	225.94
45	46.94	160	149.58	290	232.97
50	53.64	170	155.94	300	240.25
55	60.12	180	162.09	310	247.86
60	66.32	190	168.16	273.15	221.25
70	77.70	200	174.26	298.15	238.91
80	88.12	210	180.41	310.15	247.99
L-Methionine (149.2 Da) [20]					
10	2.017	90	82.68	220	157.28
15	5.883	100	89.50	230	164.14
20	11.48	110	95.90	240	172.05
25	17.79	120	101.96	250	181.13
30	24.23	130	107.70	260	192.67
35	30.65	140	113.26	270	208.28
40	36.70	150	118.66	280	229.79

Table 2 (continued)

T/K	C_P	T/K	C_P	T/K	C_P
45	42.43	160	124.01	290	259.20
50	47.87	170	129.24	300	298.28
55	53.01	180	134.47	310	298.19
60	57.91	190	139.70	273.15	214.30
70	66.99	200	145.19	298.15	290.04
80	75.19	210	151.04	310.15	296.85
L-Phenylalanine (165.2 Da) [23]					
10	2.594	90	74.73	220	152.05
15	6.682	100	80.96	230	158.49
20	11.87	110	86.94	240	165.02
25	17.36	120	92.72	250	171.54
30	23.16	130	98.49	260	178.07
35	28.93	140	104.31	270	184.60
40	34.36	150	110.17	280	191.13
45	39.44	160	116.11	290	197.69
50	44.23	170	122.01	300	204.22
55	48.74	180	127.95	310	210.71
60	53.01	190	133.93	273.15	186.65
70	60.79	200	139.87	298.15	203.01
80	67.99	210	145.85	310.15	210.79
L-Proline (115.1 Da) [23]					
10	1.301	90	59.08	220	116.06
15	4.105	100	63.60	230	120.50
20	8.314	110	67.91	240	124.93
25	13.01	120	72.17	250	129.33
30	17.85	130	76.36	260	133.85
35	22.65	140	80.63	270	138.16
40	27.17	150	84.98	280	142.67
45	31.42	160	89.45	290	147.28
50	35.38	170	93.93	300	152.09
55	39.02	180	98.41	310	156.98
60	42.43	190	102.84	273.15	141.00
70	48.62	200	107.24	298.15	151.17
80	54.10	210	111.63	310.15	157.07
L-Serine (105.1 Da) [24]					
10	0.816	90	55.90	220	107.78
15	2.703	100	61.09	230	111.25
20	5.556	110	65.73	240	114.77
25	9.063	120	70.12	250	118.28
30	13.03	130	74.35	260	121.84
35	17.21	140	78.41	270	125.39
40	21.46	150	82.34	280	128.99
45	25.63	160	86.11	290	132.59
50	29.69	170	89.83	300	136.23
55	33.59	180	93.47	310	139.91
60	37.31	190	97.11	273.15	126.52
70	44.18	200	100.67	298.15	135.56
80	50.33	210	104.22	310.15	140.00
L-Tryptophane (204.2 Da) [23]					
10	4.393	90	84.56	220	178.20
15	10.02	100	91.92	230	185.69
20	16.51	110	99.04	240	193.34

Table 2 (continued)

T/K	C_P	T/K	C_P	T/K	C_P
25	23.04	120	106.06	250	201.08
30	29.35	130	113.18	260	208.87
35	35.28	140	120.33	270	216.52
40	40.78	150	127.45	280	224.22
45	45.61	160	134.64	290	231.92
50	51.00	170	141.80	300	239.58
55	55.73	180	148.99	310	247.32
60	60.17	190	156.27	273.15	218.95
70	68.70	200	163.59	298.15	238.15
80	76.86	210	170.88	310.15	247.44
L-Tyrosine (181.2 Da) [23]					
10	1.389	90	75.06	220	162.72
15	3.908	100	82.05	230	169.45
20	7.724	110	88.83	240	176.23
25	12.57	120	95.56	250	183.05
30	18.07	130	102.26	260	189.91
35	23.91	140	108.87	270	196.86
40	29.62	150	115.52	280	203.84
45	35.24	160	122.26	290	210.79
50	40.59	170	128.99	300	217.74
55	45.56	180	135.77	310	224.60
60	50.29	190	142.38	273.15	199.08
70	59.20	200	149.12	298.15	216.44
80	67.49	210	155.81	310.15	224.72
L-Valine (117.2 Da) [22]					
10	1.100	90	64.73	220	133.01
15	3.192	100	71.34	230	137.57
20	6.615	110	77.57	240	142.05
25	10.69	120	83.55	250	146.61
30	15.18	130	89.16	260	151.17
35	19.86	140	94.56	270	155.85
40	24.46	150	99.83	280	160.50
45	29.04	160	104.98	290	165.06
50	33.50	170	109.91	300	169.70
55	37.87	180	114.73	310	174.31
60	42.09	190	119.37	273.15	157.28
70	50.04	200	123.89	298.15	168.82
80	57.61	210	128.41	310.15	174.39

Amino acid/peptide (m.w.)	C_P (298.15 K)	Reference
DL-alanine (89.1)	121.6	[25]
DL-α-amino-n-butiric acid (103.1)	146.4	[25]
D-arginine (174.2)	233.5	[26]
L-asparagine (132.1)	160.2	[26]
DL-citrulline (175.2)	231.0	[26]
D-glutamic acid·HCl	209.2	[26]
L-hydroxyproline (131.1)	153.9	[26]
L-hydroxyproline (deuterated) (133.1)	164.8	[26]
DL-ornithine (132.12)	190.8	[26]
DL-serine (105.1)	132.4	[25]
L-threonine (199.1)	147.3	[26]
DL-alanylglycine (146.2)	182.4	[26]
DL-leucylglycine (188.3)	256.5	[26]

Table 3

(A) Heat capacities (J K^{-1} mol^{-1}) of solid poly(amino acids)[a]

T/K	Poly-amino acid								
	P-Ala	P-Arg · HCl	P-Asn	P-Asp · Na	P-Glu · Na	P-Gly	P-His	P-His · HCl	P-Leu
220	–	186.40	109.30	118.80	117.70	–	104.80	127.90	132.80
230	78.33	192.20	112.40	122.10	124.30	53.00	108.40	133.80	137.80
240	79.04	198.60	115.20	126.10	129.60	54.80	114.40	139.90	142.10
250	80.96	204.90	119.40	129.60	135.10	56.60	119.60	145.90	147.00
260	83.09	211.80	123.10	133.70	139.60	58.80	124.70	151.90	151.60
270	85.51	218.10	127.20	138.00	143.90	60.50	131.00	158.80	156.30
280	88.07	224.30	131.10	142.10	148.40	62.20	136.00	164.80	161.90
290	90.70	230.30	135.00	146.20	152.70	64.58	141.50	170.70	168.60
300	93.47	236.30	139.00	150.80	157.40	66.75	147.90	177.60	175.80
310	96.24	242.30	143.30	155.20	162.10	68.80	153.30	185.50	183.80
320	99.08	249.00	147.20	159.30	167.00	70.86	160.20	191.10	189.40
330	101.80	256.00	151.30	163.60	171.90	73.02	166.00	197.20	191.90
340	104.40	263.50	155.70	168.00	177.70	75.19	171.70	203.10	193.00
350	106.50	269.60	159.40	171.80	182.90	77.36	177.40	208.90	195.20
360	108.80	276.60	163.20	175.50	188.90	79.53	182.40	214.90	199.60
370	111.20	282.00	167.40	180.00	195.60	81.75	186.10	220.80	204.60
380	113.30	290.40	171.40	185.00	201.00	84.09	192.10	226.50	209.80
390	115.30	298.00	175.40	189.90	206.70	86.49	197.90	232.50	215.90

Heat capacities (J K^{-1} mol^{-1}) of solid poly(amino acids)[b]

T/K	Poly-amino acid							
	P-Lys · HBr	P-Met	P-Phe	P-Pro	P-Ser	P-Trp	P-Tyr	P-Val
220	165.10	122.80	122.10	89.20	83.50	132.70	133.00	–
230	171.10	127.50	127.20	92.56	86.90	140.30	137.90	120.20
240	176.80	132.50	132.00	95.34	89.91	146.70	142.80	123.10
250	182.70	139.30	137.60	98.60	93.19	153.30	148.60	126.20
260	188.10	146.80	143.60	102.40	96.74	160.10	154.80	129.60
270	193.50	154.30	149.90	105.50	100.80	167.10	161.60	133.00
280	198.60	161.80	156.40	109.10	104.80	174.90	169.10	136.80
290	203.40	169.40	163.20	112.20	109.00	183.00	176.30	140.60
300	208.50	176.70	169.70	115.70	112.90	190.60	183.60	144.20
310	213.60	184.00	176.20	119.20	117.10	199.00	191.40	148.40
320	218.20	190.80	183.10	122.90	121.30	207.20	199.60	152.00
330	223.70	197.50	189.70	126.60	125.60	215.90	207.20	155.90
340	229.50	203.60	196.80	130.50	129.80	225.10	215.70	159.60
350	234.50	209.30	203.40	134.20	134.20	233.30	223.40	163.30
360	240.90	215.40	209.60	137.70	139.80	241.50	229.90	166.70
370	247.90	221.20	215.80	141.90	143.90	250.00	236.70	170.90
380	255.30	226.40	221.70	146.00	148.00	258.90	243.60	174.80
390	263.90	232.00	227.80	149.60	152.10	269.20	249.50	178.60

(B) Heat capacities (J K^{-1} mol^{-1}) of solid copoly(amino acids)[c]

T/K	Copoly-amino acid			
	P-(Lys · HBr/Ala)	P-(Lys · HBr/Phe)	P-(Na · Glu/Tyr)	P-(Pro-Gly-Pro)
220	237.90	272.70	258.90	223.30
230	245.20	284.60	267.70	231.90
240	251.80	294.60	277.40	240.40
250	258.50	306.50	288.40	249.30

Table 3 (continued)

T/K	Copoly-amino acid			
	P-(Lys · HBr/Ala)	P-(Lys · HBr/Phe)	P-(Na · Glu/Tyr)	P-(Pro-Gly-Pro)
260	266.20	317.60	303.00	259.40
270	273.40	330.40	313.70	268.60
280	281.60	342.50	325.90	279.00
290	289.80	354.90	339.20	289.70
300	297.50	366.50	353.20	300.10
310	305.90	380.20	362.90	310.50
320	313.20	392.30	378.60	321.20
330	321.00	403.50	392.20	331.80
340	328.20	416.90	406.80	342.60
350	335.00	431.60	420.50	352.40
360	342.70	447.60	430.70	362.80
370	349.90	460.00	440.70	372.70
380	356.40	472.70	452.30	382.50
390	363.10	485.40	461.80	392.20

[a] Poly-L-Alanine (m.w. 15,000 Da) [27]; Poly-L-Arginine · HCl (m.w. 132,000 Da) [28]; Poly-L-Aspartic acid · Na (m.w. 42,500 Da) [28]; Poly-L-Asparagine (m.w. 10,400 Da) [28]; Poly-L-Glutamic Acid · Na (m.w. 74,000 Da) [28]; Poly-Glycine II (m.w. 15,000 Da) [27]; Poly-L-Histidine (m.w. 49,000 Da) [28]; Poly-L-Histidine HCl (m.w. 139,200 Da) [28]; Poly-L-Leucine (m.w. 150,000 Da) [28].

[b] Poly-L-Lysine · HBr (m.w. 560,000 Da) [28]; Poly-L-Methionine (m.w. 160,000 Da) [28]; Poly-L-Phenylalanine (m.w. 23,000 Da) [28]; Poly-L-Proline (m.w. 44,000 Da) [28]; Poly-L-Serine (m.w. 6000 Da) [28]; Poly-L-Tryptophane (m.w. 160,000 Da) [28]; Poly-L-Tyrosine (m.w. 125,000 Da) [28]; Poly-L-Valine (m.w. 7230 Da) [27].

[c] Poly(L-Lysine · HBr-Alanine) (molar ratio 46/54, m.w 37,000 Da) [29]; Poly(L-Lysine · HBr-Phenylalanine) (molar ratio 51/49, m.w 49,700 Da) [29]; Poly(L-Glutamic Acid · Na-Tyrosine) (molar ratio 50/50, m.w 30,000 Da) [29]; Poly(L-Proline-Glycine-Proline) (molar ratio 66/34, m.w 5300 Da) [29].

given concentration of solute w_i and the partial heat capacities are connected by the following equation:

$$C_{P,\phi_i} = C^0_{P,\phi_i} + \frac{\partial C_{P,\phi_i}}{\partial w_i} \cdot w_i \qquad (9)$$

At low concentrations ($\sim 10^{-2}$–10^{-3} M) the term $\{\partial C_{P,\phi_i}\}/\{\partial w_i\} \cdot w_i$ is close to zero and the apparent and partial heat capacities have the same values.

3. Instrumentation

Currently most measurements of the heat capacity of anhydrous and hydrated amino acids, peptides, polypeptides and proteins are performed by various modifications of the adiabatic absolute calorimeters [11–13]. The operational principle of these calorimeters is based on the 'heat-pulse' method. A definite amount of thermal energy (ΔQ) is provided to an isolated sample and the temperature rise (ΔT) is determined. The heat capacity is defined as:

$$C_P = \lim_{\Delta T \to 0} \frac{\Delta Q}{\Delta T} \qquad (10)$$

In practice, ΔT has a finite value and the measured heat capacity corresponds to the midpoint of the ΔT interval. An advantage of this method is that a sample is in thermal equilibrium before and after applying the heat and, thus, the heat capacity is determined at equilibrium conditions. By repeating this procedure many times, one can get the heat capacity values in a broad temperature range. Adiabatic absolute calorimeters provide very high precision of the heat capacity measurements but require a large amount of material.

Table 4
Heat capacities (J K^{-1} g^{-1}) of anhydrous and hydrated proteins

T/K	$C_P \times 10^2$	T/K	$C_P \times 10^2$	T/K	$C_P \times 10^2$
Anhydrous bovine zinc insulin (5665 Da) [30]					
10	1.987	90	45.56	220	94.73
15	4.427	100	49.87	230	98.58
20	7.305	110	53.93	240	102.42
25	10.42	120	57.78	250	106.32
30	13.64	130	61.51	260	110.21
35	16.86	140	65.27	270	114.14
40	19.95	150	69.04	280	118.03
45	22.90	160	72.80	290	122.05
50	25.74	170	76.53	300	126.11
55	28.48	180	80.21	310	130.25
60	31.14	190	83.81	273.15	115.35
70	36.21	200	87.40	298.15	125.35
80	41.00	210	91.04	310.15	130.29
Hydrated (4.0% H_2O) bovine zinc insulin (5665 Da) [30]					
10	1.933	90	46.94	220	98.95
15	4.339	100	51.25	230	103.01
20	7.284	110	55.40	240	107.07
25	10.49	120	59.41	250	111.21
30	13.89	130	63.39	260	115.44
35	17.23	140	67.32	270	119.75
40	20.46	150	71.30	280	124.10
45	23.56	160	75.23	290	128.45
50	26.55	170	79.20	300	132.84
55	29.43	180	83.14	310	137.24
60	32.20	190	87.03	273.15	121.13
70	37.46	200	90.96	298.15	132.01
80	42.38	210	94.94	310.15	137.28
Anhydrous bovine chymotrypsinogen (25,666 Da) [30]					
10	1.874	90	46.86	220	97.82
15	4.343	100	51.09	230	101.67
20	7.297	110	55.31	240	105.56
25	10.53	120	59.33	250	109.50
30	13.87	130	63.26	260	113.55
35	17.15	140	67.15	270	117.57
40	20.33	150	70.96	280	121.67
45	23.38	160	74.77	290	125.86
50	26.39	170	78.58	300	130.08
55	29.34	180	82.43	310	134.27
60	32.19	190	86.23	273.15	118.87
70	37.48	200	90.08	298.15	129.29
80	42.26	210	93.97	310.15	134.35
Hydrated (10.7% H_2O) bovine chymotrypsinogen (25,666 Da) [30]					
10	1.778	90	51.13	220	114.56
15	4.184	100	55.98	230	120.16
20	7.309	110	60.71	240	125.86
25	10.84	120	65.44	250	131.59
30	14.43	130	70.12	260	137.40
35	18.06	140	74.81	270	143.30
40	21.61	150	79.50	280	149.24
45	25.03	160	84.22	290	155.23

Table 4 (continued)

T/K	$C_P \times 10^2$	T/K	$C_P \times 10^2$	T/K	$C_P \times 10^2$
50	28.28	170	88.95	300	161.34
55	31.45	180	93.76	310	167.11
60	34.55	190	98.70	273.15	145.35
70	40.45	200	103.85	298.15	160.42
80	45.94	210	109.12	310.15	167.40
Anhydrous native bovine serum albumin (66,433 Da) [8]					
10	1.854	90	46.23	220	96.48
15	4.234	100	50.54	230	100.25
20	7.058	110	54.69	240	104.01
25	10.14	120	58.74	250	107.91
30	13.36	130	62.63	260	111.88
35	16.60	140	66.44	270	115.90
40	19.72	150	70.25	280	119.96
45	22.71	160	74.06	290	124.14
50	25.71	170	77.82	300	128.32
55	28.61	180	81.59	310	132.55
60	31.37	190	85.31		
70	36.62	200	89.08		
80	41.59	210	92.80		
Anhydrous denatured bovine serum albumin (66,433 Da) [8]					
10	1.866	90	46.44	220	97.15
15	4.272	100	50.79	230	101.04
20	7.176	110	54.94	240	105.02
25	10.36	120	58.99	250	109.08
30	13.62	130	62.93	260	113.22
35	16.87	140	66.78	270	117.45
40	20.00	150	70.63	280	121.71
45	23.05	160	74.43	290	126.02
50	26.08	170	78.20	300	130.37
55	29.06	180	81.92	310	134.77
60	31.92	190	85.69	273.15	118.78
70	37.10	200	89.50	298.15	129.54
80	41.88	210	93.30	310.15	134.81
Hydrated (2.14% H_2O) bovine serum albumin (66,433 Da) [8]					
10	1.678	90	47.07	220	99.75
15	4.038	100	51.46	230	103.81
20	7.079	110	55.65	240	107.86
25	10.54	120	59.75	250	111.92
30	13.70	130	63.68	260	116.06
35	16.96	140	67.66	270	120.33
40	20.11	150	71.67	280	124.52
45	23.18	160	75.73	290	128.78
50	26.20	170	79.75	300	133.05
55	29.09	180	84.31	310	137.28
60	31.90	190	87.70		
70	37.29	200	91.71		
80	42.34	210	95.73		
Anhydrous bovine serosal collagen (280,950 Da) [8]					
10	1.774	90	45.10	220	93.09
15	4.105	100	49.20	230	96.65
20	6.891	110	53.22	240	100.25

Table 4 (continued)

T/K	$C_P \times 10^2$	T/K	$C_P \times 10^2$	T/K	$C_P \times 10^2$
25	10.00	120	57.11	250	103.93
30	13.18	130	60.88	260	107.70
35	16.33	140	64.56	270	111.46
40	19.42	150	68.16	280	115.31
45	22.37	160	71.71	290	119.12
50	25.28	170	75.23	300	122.93
55	28.07	180	78.83	310	126.73
60	30.77	190	82.43	273.15	112.68
70	35.94	200	86.02	298.15	122.22
80	40.71	210	89.58	310.15	126.78
Hydrated (13.53% H_2O) bovine serosal collagen (280,950 Da) [8]					
10	1.536	90	50.63	220	113.60
15	3.895	100	55.52	230	118.95
20	6.945	110	60.25	240	124.52
25	10.41	120	64.94	250	130.29
30	14.00	130	69.58	260	136.23
35	17.68	140	74.35	270	142.34
40	21.26	150	78.87	280	148.57
45	24.53	160	83.55	290	155.02
50	27.86	170	88.28	300	161.63
55	31.10	180	93.09	310	168.41
60	34.16	190	98.07	273.15	144.31
70	39.95	200	103.14	298.15	160.42
80	45.44	210	108.32	310.15	168.49

Protein (m.w)	C_P(298.15 K)	Reference
Zn-insulin (5665)	1.254	[30]
Serum albumin (66,446)	1.275	[8]
α-Chymotrypsinogen (25,666)	1.293	[30]
Lysosyme (14,300)	1.494	[31]
Ovalbumin (42,750)	1.534	[31]
Collagen (280,950)	1.222	[8]
Keratin (54,000)	1.264	[13]

Rat tail tendon collagen at different water content, R (grams of water per gram of protein) [32]

R (g/g)	Temperature (°C)				
	−60	−40	−20	0	20
Before denaturation					
1.44	1.582	1.778	2.343	3.033	3.117
1.01	1.548	1.849	2.469	2.816	2.908
0.93	1.598	1.891	2.510	2.812	2.900
0.79	1.582	1.862	2.594	2.669	2.812
0.65	1.556	1.841	2.803	2.481	2.586
0.527	1.577	1.883	2.761	2.339	2.43
0.468	1.498	1.799	2.803	2.259	2.335
0.428	1.494	1.757	2.469	2.176	2.247
0.376	1.381	1.715	1.925	2.000	2.155
1.44	1.623	1.778	2.343	3.054	3.138
After denaturation					
1.44	1.674	1.904	2.929	3.293	3.548
1.02	1.686	1.946	3.347	3.138	3.439

Table 4 (continued)

R (g/g)	Temperature (°C)				
	−60	−40	−20	0	20
0.93	1.695	1.950	3.766	2.966	3.314
0.79	1.715	2.029	3.347	2.862	3.264
0.651	1.715	2.050	3.347	2.715	3.130
0.524	1.766	2.121	3.347	2.607	2.853
0.468	1.674	2.033	3.347	2.552	2.778
0.428	1.582	1.941	2.510	2.481	2.653
0.375	1.464	1.799	2.929	2.393	2.569

Keratin (merino wool) [13]

T/°C	Water content (% of weight of keratin)									
	0	2.8	7.6	10.4	16.9	20.9	24.8	28.4	30.7	33.9
−70	0.887	0.925	1.004	1.013	1.088	1.176	1.230	1.247	1.264	1.230
−60	0.929	0.971	1.059	1.067	1.159	1.255	1.322	1.351	1.364	1.343
−50	0.971	1.013	1.109	1.121	1.234	1.335	1.414	1.456	1.464	1.460
−40	1.008	1.054	1.159	1.176	1.305	1.414	1.506	1.561	1.565	1.573
−30	1.046	1.096	1.213	1.230	1.377	1.494	1.607	1.665	1.682	1.674
−20	1.088	1.142	1.264	1.280	1.448	1.577	1.715	–	–	–
−10	1.125	1.184	1.318	1.335	1.519	1.657	1.787	–	–	–
0	1.167	1.226	1.368	1.393	1.590	1.745	1.883	1.992	2.063	2.079
10	1.205	1.272	1.423	1.452	1.665	1.837	1.975	2.079	2.146	2.159
20	1.243	1.314	1.473	1.523	1.745	1.933	2.067	2.167	2.230	2.234
30	1.284	1.356	1.527	1.594	1.837	2.050	2.197	2.255	2.310	2.318
40	1.322	1.402	1.582	1.665	1.933	2.142	2.255	2.330	–	2.356
50	1.364	1.443	1.636	1.732	2.025	2.201	2.310	2.372	–	2.393
60	1.402	1.494	1.695	1.803	2.105	2.255	2.356	2.402	2.460	2.439
70	1.443	1.540	1.757	1.879	2.180	2.314	2.402	2.439	2.494	2.481
80	1.481	1.590	1.820	1.962	2.238	2.360	2.448	2.494	2.540	2.519
90	1.523	1.640	1.887	2.054	2.293	2.406	2.494	2.540	–	2.556
100	1.561	1.690	1.950	2.151	2.330	2.448	2.536	2.586	–	2.602

The ‘heat-pulse’ method is also the basis of drop [14] and flow [15,16] calorimeters which provide an estimation of the heat capacity at fixed temperatures. A drop calorimeter operation consists in dropping a preliminarily thermostated ampoule containing the sample into the isothermal calorimeter. A great advantage of this calorimeter is the ability to obtain heat capacity measurements not only of solid but also of liquid samples (e.g., solutions). In contrast, by using flow calorimetry, one can measure only liquid samples which are preliminarily heated in the thermostat, located above the calorimeter, and then pumped into the calorimetric cell. Both drop and flow calorimeters provide measurements of the heat capacity value with quite a high precision (detection limit 10^{-5} J K^{-1} cm^{-3}), but only at an appointed temperature.

Heat capacity measurements of solutions over a broad temperature range of 0 to 150°C are performed by adiabatic scanning microcalorimeters. The operation mode of these calorimeters is the so-called ‘continuous heating’ method. The main principle of this method is to supply thermal energy with a constant rate $V = dQ/dt$, and follow a rise in temperature. The heat capacity is defined as:

$$C_P = \frac{V}{(dT/dt)} \tag{11}$$

This method is employed in the differential adiabatic scanning microcalorimeters [17] operating in the temperature range of 250–400 K and having the highest precision of the relative heat capacity determination (10^{-5} J K^{-1}). The absolute value of the partial heat capacity can be determined using adia-

Table 5
Partial heat capacities (J K^{-1} mol^{-1}) of amino acids in aqueous solutions

Amino acid	Solvent	Method	T°C	$C^0_{P,\phi}$	Reference
DL-α-Abu m.w. 103.1	Water	FC	25	234.1(1.0)	[33]
	0.5 M Glucose	FC	25	239.0(2.3)	[34]
	1 M Glucose	FC	25	239.1(2.3)	[34]
	0.5 M Sucrose	FC	25	240.7(1.4)	[34]
	1 M Sucrose	FC	25	242.5(1.4)	[34]
	1 M Glycerol	FC	25	229.9(1.0)	[33]
	1 M Mannitol	FC	25	235.9(1.0)	[33]
	1 M Sorbitol	FC	25	238.5(1.0)	[33]
	1 M NaCl	FC	25	252.3(3.4)	[35]
	3 M NaCl	FC	25	270.5(3.8)	[35]
	1 M $CaCl_2$	FC	25	271.6(2.4)	[36]
β-Abu m.w. 103.1	Water	DC	25	164.4(4.2)[a]	[37]
		DC	32	162.3(8.4)[a]	[37]
γ-Abu m.w. 103.1	Water	DC	25	134.3(8.4)[a]	[37]
		DC	32	137.7(8.4)[a]	[37]
β-Ala m.w. 89.1	Water	DC	25	81.2(8.4)[a]	[37]
		DC	32	91.2(8.4)[a]	[37]
D-Ala m.w. 89.1	Water	FC	25	144.7(1.0)	[33]
	1 M Mannitol	FC	25	154.3(1.0)	[33]
	1 M Sorbitol	FC	25	158.2(1.0)	[33]
DL-Ala m.w. 89.1	Water	DC	25	147.7(2.1)[a]	[37]
		DC	32	153.6(2.1)[a]	[37]
	0.5 M Glucose	FC	25	152.2(1.8)	[34]
	1 M Glucose	FC	25	156.7(1.8)	[34]
	0.5 M Sucrose	FC	25	154.3(1.1)	[34]
	1 M Sucrose	FC	25	157.3(1.1)	[34]
	1 M NaCl	FC	25	165.4(2.0)	[35]
	3 M NaCl	FC	25	191.7(1.6)	[35]
	1 M $CaCl_2$	FC	25	201.7(1.3)	[36]
L-Ala m.w. 89.1	Water	FC	25	141.4(0.2)	[38]
	1 M Urea	FC	25	152.9(0.3)[a]	[39]
	3.01 M Urea	FC	25	169.2(0.5)[a]	[39]
	4.88 M Urea	FC	25	180.0(1.0)[a]	[39]
	7 M Urea	FC	25	189.1(0.1)	[39]
	7.97 M Urea	FC	25	192.6(0.7)[a]	[39]
	8 M Urea	FC	25	195.2(0.5)	[38]
	1 M Glycerol	FC	25	144.4(1.0)	[33]
	1 M Mannitol	FC	25	155.5(1.0)	[33]
	1 M Sorbitol	FC	25	159.0(1.0)	[33]
acetyl-Ala-amide m.w. 132.1	Water	FC	25	346.4(0.6)	[40]
L-Arg m.w. 174.2	Water	FC	25	279(1)	[38]
	8 M Urea	FC	25	381(1)	[38]
L-Asn m.w. 132.1	Water	FC	25	125(1)	[38]
	8 M Urea	FC	25	254(2)	[38]
L-Asp m.w. 133.1	Water	FC	25	127(4)	[38]
	8 M Urea	FC	25	231(9)	[38]
L-CysH m.w. 121.2	Water	FC	25	188.0(0.2)	[38]
	8 M Urea	FC	25	232.1(1.6)	[38]
L-Gln m.w. 146.1	Water	FC	25	187(1)	[38]
	8 M Urea	FC	25	290(3)	[38]
L-Glu m.w. 147.1	Water	FC	25	177(4)	[38]
	8 M Urea	FC	25	290(4)	[38]

Table 5 (continued)

Amino acid	Solvent	Method	T°C	$C^0_{P,\phi}$	Reference
Gly m.w. 75.1	Water	FC	25	39.2(0.4)	[38]
	1 M Urea	FC	25	60.2(0.5)[a]	[39]
	3.01 M Urea	FC	25	87.8(0.4)[a]	[39]
	4.88 M Urea	FC	25	105.4(1.2)[a]	[39]
	7 M Urea	FC	25	121.8(0.2)	[39]
	7.97 M Urea	FC	25	128.1(0.3)[a]	[39]
	8 M Urea	FC	25	133.1(0.4)	[38]
	0.5 M Glucose	FC	25	54.2(0.3)	[34]
	1 M Glucose	FC	25	65.4(0.3)	[34]
	0.5 M Sucrose	FC	25	62.5(0.6)	[34]
	1 M Sucrose	FC	25	74.9(0.6)	[34]
	1 M Glycerol	FC	25	49.4(1.0)	[33]
	1 M Mannitol	FC	25	60.2(1.0)	[33]
	1 M Sorbitol	FC	25	63.5(1.0)	[33]
	1 M NaCl	FC	25	84.7(1.0)	[35]
	2 M NaCl	FC	25	108.4(1.9)	[35]
	3 M NaCl	FC	25	116.3(0.9)	[35]
	4 M NaCl	FC	25	126.9(2.0)	[35]
	1 M $CaCl_2$	FC	25	117.4(2.6)	[36]
acetyl-Gly-amide m.w. 118.1	Water	FC	25	238.4(0.5)	[40]
N-methyl-Gly m.w. 89.1	Water	DC	25	105.0(6.3)[a]	[37]
		DC	32	112.1(6.3)[a]	[37]
N,*N*-dimethyl-Gly m.w. 103.1	Water	DC	25	182.8(8.4)[a]	[37]
		DC	32	201.7(8.4)[a]	[37]
L-His m.w. 155.2	Water	FC	25	241(1)	[38]
	8 M Urea	FC	25	329(2)	[38]
L-Ile m.w. 131.2	Water	FC	25	383.3(0.4)	[38]
	8 M Urea	FC	25	362(7)	[38]
L-Leu m.w. 131.2	Water	FC	25	397.7(1.2)	[38]
	8 M Urea	FC	25	360(2)	[38]
	1 M NaCl	FC	25	420.4(2.6)	[35]
	3 M NaCl	FC	25	418.2(5.2)	[35]
	1 M $CaCl_2$	FC	25	442.7(2.4)	[36]
	1 M Glucose	FC	25	401.7(2.2)	[34]
	1 M Sucrose	FC	25	402.4(3.0)	[34]
L-Lys m.w. 146.2	Water	FC	25	267(5)	[38]
	8 M Urea	FC	25	337(2)	[38]
L-Met m.w. 149.2	Water	FC	25	293(29)	[38]
	8 M Urea	FC	25	317.4(0.9)	[38]
DL-Nleu m.w. 131.2	Water	FC	25	404.5(3.0)	[33]
	Water				
DL-Nval m.w. 117.2	Water	FC	25	320.2(1.0)	[33]
	1 M Glycerol	FC	25	315.0(1.0)	[33]
L-Phe m.w. 165.2	Water	FC	25	384(2)	[38]
	8 M Urea	FC	25	393.6(2.8)	[38]
L-Pro m.w. 115.1	Water	FC	25	172.3(0.9)	[38]
	8 M Urea	FC	25	214.0(1.8)	[38]
L-Ser m.w. 105.1	Water	FC	25	117.4(0.1)	[38]
	1 M Urea	FC	25	137.9(0.5)[a]	[39]
	3.01 M Urea	FC	25	168.8(1.0)[a]	[39]
	4.88 M Urea	FC	25	189.8(0.5)[a]	[39]
	7 M Urea	FC	25	210.1(0.2)	[39]
	7.97 M Urea	FC	25	204.6(5.5)[a]	[39]
	8 M Urea	FC	25	219.5(0.6)	[38]

Table 5 (continued)

Amino acid	Solvent	Method	T°C	$C^0_{P,\phi}$	Reference
	Water	DC	25	115.1(8.4)[a]	[37]
	Water	DC	32	117.2(8.4)[a]	[37]
L-Thr m.w. 119.1	Water	FC	25	210(2)	[38]
	8 M Urea	FC	25	283.7(0.6)	[38]
	Water	DC	25	208.4(8.4)[a]	[37]
	Water	DC	32	210.0(12.6)[a]	[37]
L-Trp m.w. 264.2	Water	FC	25	420(13)	[38]
	8 M Urea	FC	25	445.6(5.6)	[38]
L-Tyr m.w. 181.2	Water	FC	25	299(20)	[38]
	8 M Urea	FC	25	312(30)	[38]
L-Val m.w. 117.2	Water	FC	25	301.9(1.0)	[38]
	8 M Urea	FC	25	301.2(0.4)	[38]
	0.5 M Glucose	FC	25	308.2(1.0)	[34]
	1 M Glucose	FC	25	311.5(1.0)	[34]
	0.5 M Sucrose	FC	25	309.8(1.0)	[34]
	1 M Sucrose	FC	25	311.5(1.0)	[34]
	1 M Glycerol	FC	25	302.6(1.0)	[33]
	1 M Mannitol	FC	25	310.9(1.0)	[33]
	1 M Sorbitol	FC	25	311.8(1.0)	[33]
	1 M NaCl	FC	25	330.0(2.8)	[35]
	3 M NaCl	FC	25	339.0(6.9)	[35]
	1 M $CaCl_2$	FC	25	348.4(1.5)	[36]
	Water	DC	25	284.5(8.4)[a]	[37]
	Water	DC	32	287.4(8.4)[a]	[37]
D-Val m.w. 117.2	Water	FC	25	307.8(1.0)	[33]
	1 M Mannitol	FC	25	309.6(1.0)	[33]
	1 M Sorbitol	FC	25	310.9(1.0)	[33]

[a] These values represent not partial, $C^0_{P,\phi}$, but apparent, $C_{P,\phi}$, values.

batic differential scanning microcalorimetry with an accuracy of about 3%.

4. Description of the data

Molar heat capacities of solid amino acids and peptides are presented in Tables 1 and 2. Table 3 presents molar heat capacities of polyamino acids. Specific heat capacities of anhydrous and hydrated proteins are presented in Table 4. All of the measurements were done by using adiabatic absolute calorimetry and their accuracy is better than 1–2%.

Tables 5–7 summarize the partial heat capacities of amino acids, peptides and proteins in aqueous solution. The tables provide for each compound the molecular mass, solvent conditions, type of calorimetry used for measurements (DSC—differential adiabatic scanning microcalorimetry, FC—flow calorimetry, DC—drop calorimetry), reference temperature, experimental values of the partial heat capacity and source of data. Entries in parentheses of the $C^0_{P,\phi}$ values show the precision of the partial heat capacity determination.

Table 5 and 6 present partial molar heat capacities of amino acids, peptides and their derivatives in various solvents. Most of the listed data are obtained by the drop and the flow calorimetry and are available only in the temperature range of 25–30°C. For some peptides studied by the differential adiabatic scanning microcalorimetry, the $C^0_{P,\phi}$ values are available in the temperature range 5–125°C. All amino acids and peptides are listed alphabetically using the three letter symbols of amino acids and the established abbreviations, beginning with the N-terminals. Derivatives of amino acids and peptides are listed together with the parent compounds.

Table 7 presents partial specific heat capacities of a number of proteins in the native and denatured states. Proteins are listed alphabetically by trivial

Table 6
Partial heat capacities (J K^{-1} mol^{-1}) of peptides in aqueous solution

Amino acid	Solvent	Method	T°C	$C^0_{P,\phi}$	Reference
Ala–Ala m.w. 160.2	Water	FC	25	330.8(0.4)	[41]
	7 M Urea	FC	25	384.1(0.2)	[39]
cyclo(Ala–Ala) m.w. 142.2	Water	DSC	5	280.7(7.4)	[42]
		DSC	25	321.7(7.4)	[42]
		DSC	50	360.7(7.4)	[42]
		DSC	75	388.2(7.4)	[42]
		DSC	100	407.6(7.4)	[42]
		DSC	125	416.9(7.4)	[42]
acetyl-Ala–Ala-amide m.w. 203.2	Water	FC	25	537.5(0.7)	[40]
Ala–Ala–Ala m.w. 231.3	Water	FC	25	526(1)	[41]
	7 M Urea	FC	25	585.8(0.7)	[39]
Ala–Ala–Ala–Ala m.w. 302.4	Water	FC	25	733.4(0.9)	[41]
	7 M Urea	FC	25	766.4(1.6)	[39]
acetyl-Ala-Gly-amide m.w. 189.2	Water	FC	25	430.9(0.4)	[40]
DL-Ala-Gly m.w. 146.2	Water	FC	25	203.4(0.5)	[40]
DL-Ala-Gly–Gly m.w. 203.3	Water	FC	25	286.2(0.4)	[43]
Gly-DL-Ala m.w. 146.2	Water	FC	25	219.7(6.5)	[35]
		FC	25	216.2(0.3)	[40]
	1 M NaCl	FC	25	276.8(1.4)	[35]
	1 M $CaCl_2$	FC	25	327.7(2.7)	[36]
	1 M Glucose	FC	25	242.4(1.6)	[34]
	1 M Sucrose	FC	25	252.0(2.4)	[34]
cyclo(Gly-Ala) m.w. 128.2	Water	DSC	5	186.3(6.2)	[42]
		DSC	25	235.3(6.2)	[42]
		DSC	50	273.6(6.2)	[42]
		DSC	75	307.8(6.2)	[42]
		DSC	100	330.9(6.2)	[42]
		DSC	125	344.6(6.2)	[42]
acetyl-Gly-Ala-amide m.w. 189.2	Water	FC	25	422.0(1.0)	[40]
Gly-L-Ala-Gly m.w. 203.3	Water	FC	25	289.8(0.3)	[43]
	0.5 M sodium acetate-acetic acid pH 4.0	DSC	5	215.1(13.4)	[42]
		DSC	25	252.4(13.4)	[42]
		DSC	50	343.0(13.4)	[42]
		DSC	75	405.7(13.4)	[42]
		DSC	100	471.0(13.4)	[42]
		DSC	125	530.6(13.4)	[42]
Gly-DL-α-Abu m.w. 160.2	Water	FC	25	306.2(3.6)	[35]
	1 M NaCl	FC	25	352.8(3.0)	[35]
	1 M $CaCl_2$	FC	25	397.3(4.6)	[36]
	1 M Glucose	FC	25	316.2(1.8)	[34]
	1 M Sucrose	FC	25	319.9(1.8)	[34]
Gly-L-Asn m.w. 189.2	Water	FC	25	188.1(0.4)	[44]
Gly-L-Asn-Gly m.w. 246.3	Water	FC	25	279.2(2.6)	[45]
	Water, pH 4.0	DSC	25	258.0(1.8)	[46]
	0.5 Na-Acetate, pH 4.0	DSC	25	307.5(2.2)	[46]
Gly–Gly m.w. 132.2	Water	FC	25	99.3(1.0)	[35]
	1 M Urea	FC	25	137.3(0.7)	[39]
	3.01 M Urea	FC	25	176.9(1.4)[a]	[39]
	4.88 M Urea	FC	25	201.5(1.3)[a]	[39]
	7 M Urea	FC	25	224.7(0.2)	[39]
	7.97 M Urea	FC	25	231.8(0.5)[a]	[39]

Table 6 (continued)

Amino acid	Solvent	Method	T°C	$C^0_{P,\phi}$	Reference
	0.5 M Glucose	FC	25	122.3(1.6)	[34]
	1 M Glucose	FC	25	144.4(1.6)	[34]
	0.5 M Sucrose	FC	25	140.8(2.6)	[34]
	1 M Sucrose	FC	25	160.1(2.6)	[34]
	1 M NaCl	FC	25	173.0(2.1)	[35]
	2 M NaCl	FC	25	206.5(1.6)	[35]
	3 M NaCl	FC	25	231.6(1.3)	[35]
	4 M NaCl	FC	25	245.8(1.5)	[35]
	1 M $CaCl_2$	FC	25	217.5(2.1)	[36]
acetyl-Gly–Gly-amide m.w. 175.2	Water	FC	25	322.1(0.8)	[40]
cyclo(Gly–Gly) m.w. 114.2	Water	DSC	5	88.4(5.0)	[42]
		DSC	25	138.0(5.0)	[42]
		DSC	50	184.3(5.0)	[42]
		DSC	75	220.0(5.0)	[42]
		DSC	100	245.8(5.0)	[42]
		DSC	125	270.8(5.0)	[42]
Gly–Gly-L-Ala m.w. 203.3	Water	FC	25	296.0(0.5)	[43]
Gly–Gly–Gly m.w. 189.3	Water	FC	25	188.3(0.7)	[43]
	1 M Urea	FC	25	227.5(1.4)[a]	[39]
	3.01 M Urea	FC	25	280.4(1.0)[a]	[39]
	4.88 M Urea	FC	25	312.4(0.3)[a]	[39]
	7 M Urea	FC	25	347.3(0.3)	[39]
	7.97 M Urea	FC	25	351.8(0.5)[a]	[39]
	1 M NaCl	FC	25	284.9(3.7)	[35]
	2 M NaCl	FC	25	308.8(3.1)	[35]
	1 M Glucose	FC	25	231.6(2.5)	[34]
	Water	DSC	5	98.2(5.0)	[47]
		DSC	25	175.3(5.0)	[47]
		DSC	50	239.5(5.0)	[47]
		DSC	75	285.1(5.0)	[47]
		DSC	100	322.7(5.0)	[47]
		DSC	125	360.6(5.0)	[47]
	0.5 M sodium acetate-acetic acid pH 4.0	DSC	5	93.1(11.0)	[47]
		DSC	25	194.6(11.0)	[47]
		DSC	50	275.7(11.0)	[47]
		DSC	75	348.9(11.0)	[47]
		DSC	100	413.1(11.0)	[47]
		DSC	125	474.2(11.0)	[47]
Gly–Gly–Gly–Gly m.w. 246.4	Water	FC	25	283(2)	[41]
		DSC	5	182.8(6.2)	[47]
		DSC	25	264.6(6.2)	[47]
		DSC	50	338.2(6.2)	[47]
		DSC	75	382.3(6.2)	[47]
		DSC	100	412.0(6.2)	[47]
		DSC	125	438.5(6.2)	[47]
	1 M Urea	FC	25	324.6(3.2)[a]	[39]
	3.01 M Urea	FC	25	387.1(0.5)[a]	[39]
	4.88 M Urea	FC	25	423.3(0.3)[a]	[39]
	7 M Urea	FC	25	452.7(0.5)	[39]
	7.97 M Urea	FC	25	472.2(1.6)[a]	[39]
Gly–Gly–Gly–Gly–Gly m.w. 303.5	Water	FC	25	373(6)	[41]
		DSC	5	271.3(7.4)	[47]
		DSC	25	361.7(7.4)	[47]

Table 6 (continued)

Amino acid	Solvent	Method	T°C	$C^0_{P,\phi}$	Reference
		DSC	50	430.9(7.4)	[47]
		DSC	75	473.5(7.4)	[47]
		DSC	100	497.1(7.4)	[47]
		DSC	125	520.4(7.4)	[47]
Gly-L-His-Gly m.w. 269.4	0.5 M sodium acetate-acetic acid pH 4.0	DSC	5	216.5(13.6)	[47]
		DSC	25	296.2(13.6)	[47]
		DSC	50	381.2(13.6)	[47]
		DSC	75	462.1(13.6)	[47]
		DSC	100	540.5(13.6)	[47]
		DSC	125	617.6(13.6)	[47]
	Water	FC	25	358(7)	[45]
Gly-L-Ile-Gly m.w. 246.4	0.5 M sodium acetate-acetic acid pH 4.0	DSC	5	406.5(16.0)	[42]
		DSC	25	487.8(16.0)	[42]
		DSC	50	558.1(16.0)	[42]
		DSC	75	618.0(16.0)	[42]
		DSC	100	681.4(16.0)	[42]
		DSC	125	726.8(16.0)	[42]
	Water	FC	25	530.4(0.8)	[45]
	Water, pH 5.8	DSC	25	522.8(3.7)	[46]
	Water, pH 4.0	DSC	25	483.8(3.4)	[46]
	0.5 M Na-Acetate, pH 4.0	DSC	25	509.4(3.6)	[46]
Gly-L-Leu m.w. 246.4	Water	FC	25	473.3(0.8)	[35]
	1 M NaCl	FC	25	513.9(4.6)	[35]
	1 M $CaCl_2$	FC	25	529.5(3.7)	[36]
	1 M Glucose	FC	25	476.6(3.3)	[34]
	1 M Sucrose	FC	25	482.0(1.8)	[34]
Gly-D-Leu-Gly m.w. 246.4	Water	FC	25	529.0(1.0)	[46]
Gly-L-Leu-Gly m.w. 246.4	Water	FC	25	526.1(0.7)	[46]
	0.5 M sodium acetate-acetic acid pH 4.0	DSC	5	424.2(15.6)	[42]
		DSC	25	502.8(15.6)	[42]
		DSC	50	566.6(15.6)	[42]
		DSC	75	628.3(15.6)	[42]
		DSC	100	694.7(15.6)	[42]
		DSC	125	758.7(15.6)	[42]
Gly-L-Met-Gly m.w. 263.4	0.5 M sodium acetate-acetic acid pH 4.0	DSC	5	207.9(9.0)	[47]
		DSC	25	292.5(9.0)	[47]
		DSC	50	362.1(9.0)	[47]
		DSC	75	432.8(9.0)	[47]
		DSC	100	50.35(9.0)	[47]
		DSC	125	564.7(9.0)	[47]
	Water	FC	25	429.9(1.3)	[45]
	Water, pH 5.8	DSC	25	422.6(3.0)	[46]
	Water, pH 4.0	DSC	25	393.1(2.8)	[46]
Gly-DL-Phe m.w. 222.3	Water	FC	25	422.0(0.7)	[44]
Gly-L-Phe-Gly m.w. 279.4	Water	FC	25	506.6(3.5)	[45]
Gly-L-Pro-Gly m.w. 229.3	0.5 M sodium acetate-acetic acid pH 4.0	DSC	5	161.4(11.0)	[47]
		DSC	25	230.3(11.0)	[47]
		DSC	50	292.3(11.0)	[47]
		DSC	75	361.3(11.0)	[47]
		DSC	100	425.0(11.0)	[47]
		DSC	125	486.9(11.0)	[47]
Gly-DL-Ser m.w. 162.2	Water	FC	25	161.2(0.4)	[44]
Gly-DL-Ser-Gly m.w. 219.3	Water	FC	25	263.0(1.0)	[46]

Table 6 (continued)

Amino acid	Solvent	Method	T°C	$C^0_{P,\phi}$	Reference
Gly-L-Ser-Gly m.w. 219.3	0.5 M sodium acetate-acetic acid pH 4.0	DSC	5	86.4(14.2)	[42]
		DSC	25	197.8(14.2)	[42]
		DSC	50	289.7(14.2)	[42]
		DSC	75	373.9(14.2)	[42]
		DSC	100	450.7(14.2)	[42]
		DSC	125	522.4(14.2)	[42]
Gly-DL-Thr m.w. 176.2	Water	FC	25	251.0(0.4)	[44]
Gly-L-Thr-Gly m.w. 233.3	Water	FC	25	339.4(0.7)	[45]
Gly-L-Val m.w. 174.3	Water	FC	25	352.6(5.3)	[35]
	1 M NaCl	FC	25	402.6(3.7)	[35]
	1 M $CaCl_2$	FC	25	435.7(5.4)	[36]
	1 M Glucose	FC	25	368.0(3.7)	[34]
	1 M Sucrose	FC	25	365.9(1.5)	[34]
Gly-L-Val-Gly m.w. 231.4	Water	FC	25	443.6(0.7)	[46]
	0.5 M sodium acetate-acetic acid pH 4.0	DSC	5	334.5(15.0)	[42]
		DSC	25	413.0(15.0)	[42]
		DSC	50	484.2(15.0)	[42]
		DSC	75	554.9(15.0)	[42]
		DSC	100	622.9(15.0)	[42]
		DSC	125	685.6(15.0)	[42]
L-Leu-Gly m.w. 188.3	Water	FC	25	486.2(0.3)	[35]
	1 M NaCl	FC	25	510.3(3.5)	[35]
Ser–Ser m.w. 192.9	Water	FC	25	259.9(1.5)	[41]
	7 M Urea	FC	25	390.4(1.1)	[39]
Ser–Ser–Ser m.w. 279.3	Water	FC	25	398(2)	[41]
	7 M Urea	FC	25	553.7(1.8)	[39]

[a] These values represent not partial, $C^0_{P,\phi}$, but apparent, $C_{P,\phi}$, values.

names. The partial heat capacity of a protein in the denatured state is always larger than that in the native state. This is caused by the hydration of the protein internal groups, both polar and non-polar, exposed to solvent upon denaturation [62,81]. The contribution of all other factors, such as the configurational freedom gain, rupture of internal bonds, electrostatic effects, etc., does not exceed 15% of the total heat capacity change of protein denaturation.

Partial heat capacities of proteins in aqueous solution can be predicted from the amino acid composition of a protein. The partial molar heat capacity of a polypeptide chain n-residues long in an aqueous solution in a fully extended conformation can be calculated by a simple summation of the heat capacities of the protein constituent groups [62,47]:

$$C^0_{P,\phi} = (n-1)\cdot C^0_{P,\phi}(\text{–CHCONH–}) + \sum_{i=1}^{N} C^0_{P,\phi}(\text{–R}_i) \qquad (12)$$

The values for the protein constituent groups, partial molar heat capacities of peptide backbone, $C^0_{P,\phi}$ (–CHCONH–), and of all side chains, $C^0_{P,\phi}$(–R_i), are given in Table 8. Eq. (12) calculates the temperature dependence of the partial heat capacity for the unfolded polypeptide chain of any protein with a known amino acid composition. This equation has been tested on a number of different proteins and it has been shown that the deviation between predicted and experimentally determined values does not exceed 5%.

5. Concluding remarks

Heat capacities of amino acids, peptides, and proteins presented in this paper were measured using various calorimetric techniques. This area however, is becoming ‘intruded’ by both theoretical and experimental methods. Of particular interest is the possi-

Table 7
Partial heat capacities (J K^{-1} g^{-1}) of proteins in aqueous solutions

Protein(source)	Solvent	Method	T°C	$C^0_{P,\phi}$	Reference
Native state					
Adrenodoxin (bovine adrenal ferrodoxin) m.w. 14,020 holo form	40 mM glycine, 1 mM ascorbic acid, 10 mM mercaptoethanol pH 8.5	DSC	25	1.58(0.15)	[48]
Apocytochrome b5 (rabbit liver) m.w. 16,700	25 mM HEPES Na-phosphate CHES pH 7–10	DSC	20	1.57(0.12)	[49]
Apomyoglobin (sperm whale) m.w. 17,200	20 mM sodium acetate or phosphate pH 5.0–6.0	DSC	25	1.60(0.04)	[50]
Barnase (*Bacillus Amyloliquefaciens*) m.w. 12,365	10 mM glycine or acetate pH 2–6	DSC	5	1.33(0.07)	[51]
		DSC	25	1.50(0.07)	[51]
		DSC	40	1.62(0.07)	[51]
Barstar (*Bacillus amyloliquefaciens*) m.w. 10,780		DSC	20	1.59(0.13)	[52]
		DSC	20	1.33(0.14)	[53]
BPTI (bovine pancrease) m.w. 6565	10 mM glycine or acetate pH 2–5	DSC	5	1.33(0.07)	[54]
		DSC	25	1.45(0.07)	[54]
		DSC	50	1.60(0.07)	[54]
		DSC	75	1.74(0.07)	[54]
α-Chymotrypsin (porcine) m.w. 25,400	50 mM glycine or sodium phosphate pH 2–4 and 6–8	DSC	20	1.30(0.08)	[55]
	0.01 M KCl–HCl	FC	25	1.58(0.05)	[56]
	pH 4.0	FC	50	1.68(0.08)	[56]
CheY (chemotactic protein, *Escherichia coli*) m.w. 14,000	10 mM glycine, pH 2.5 and 10.3, or 10 mM sodium phosphate, pH 7.0	DSC	25	1.43(0.07)	[57]
Chymotrypsinogen (porcine) m.w. 25,670	H_2O–HCl pH 2.0	DSC	20	1.67(0.07)	[58]
	H_2O–HCl pH 2.0	DSC	25	1.72(0.07)	[58]
	Water	DC	25	1.529(0.01)	[31]
	0.01 M KCl–HCl	FC	25	1.53(0.05)	[56]
	pH 4.0	FC	50	1.73(0.09)	[56]
Collagen (pike skin) m.w. 93,000	20 mM glycine pH 3.0	DSC	25	1.35(0.04)	[50]
Cro repressor (γ phage) m.w. 14,700/dimer	10 mM acetate, pH 5.0	DSC	25	1.78(0.07)	[59]
Cytochrome b5	25 mM MOPS, HEPPS	DSC	25	1.46(0.17)	[60]
(rabbit liver) m.w. 16,700	Na-phosphate CHES pH 7–10				
Tryptic fragment (1–90) m.w. 10,933		DSC	25	1.34(0.08)	[61]
Cytochrome c (horse heart) m.w. 12,300	20 mM glycine or sodium acetate pH 3.0–6.0	DSC	5	1.29(0.04)	[62]
		DSC	25	1.42(0.04)	[62]
		DSC	50	1.60(0.04)	[62]
Ferredoxin (*Thermotoga maritima*) m.w. 6565	40 mM glycine, 10 mM sodium sulfide, 10 mM mercaptoethanol, pH 8.5	DSC	25	1.32(0.09)	[63]
Histone H1 (calf thymus) m.w. 21,503	50 mM Tris/HCl 0.5 M NaCl pH 8.0	DSC	20	1.50(0.08)	[64]
GH1 fragment (36–121) m.w. 8590	50 mM Tris/HCl 0.2 M potassium sulphate pH 8.0	DSC	20	1.21(0.08)	[64]
CH1 fragment (122–213) m.w. 9450		DSC	20	1.84(0.08)	[64]
Histone H5 (chicken erythrocytes)	50 mM Tris/HCl 0.5 NaCl pH 8.0	DSC	20	1.59(0.08)	[64]
GH5 fragment (22–100) m.w. 8903	50 mM Tris/HCl 0.2 M potassium sulphate pH 8.0	DSC	20	1.30(0.08)	[64]

Table 7 (continued)

Protein (source)	Solvent	Method	T°C	$C^0_{P,\phi}$	Reference
Interleukin-1β (human) m.w. 17,381	10 mM glycine or acetate pH 2–4	DSC	5	1.52(0.08)	[65]
		DSC	25	1.62(0.08)	[65]
		DSC	45	1.71(0.08)	[65]
α–Lactalbumin	0.4 M Imidazole, pH 6.3	DSC	25	1.65(0.08)	[66]
(bovine)	10 mM sodium acetate, pH 5.2 holo form		20	1.40(0.05)	[67]
m.w. 14,180	10 mM sodium acetate, pH 5.2 apo form		20	1.55(0.05)	[67]
Lactoperoxidase (bovine milk) m.w. 78,500	25 mM glycine or sodium acetate pH 3.0–6.0	DSC	25	1.44(0.06)	[68]
Lysozyme (hen egg) m.w. 14,314	20 mM glycine or sodium acetate pH 2.0–5.0	DSC	5	1.27(0.04)	[62]
		DSC	25	1.40(0.04)	[62]
		DSC	50	1.55(0.04)	[62]
	Water	DC	25	1.494(0.007)	[31]
Lysozyme (equine) m.w. 14,650	10 mM sodium acetate, pH 4.5	DSC	25	1.37(0.07)	[69]
MATα2 homeodomain (*Saccharomyces cerevisie*) m.w. 9748	20 mM sodium phosphate, 1 mM EDTA, pH 7.0	DSC	15	2.05(0.10)	[70]
Myoglobin (sperm whale) m.w. 17,760	20 mM sodium acetate pH 4.0–6.0	DSC	5	1.23(0.04)	[62]
		DSC	25	1.36(0.04)	[62]
		DSC	50	1.54(0.04)	[62]
Nuclease (*Staphyloccocus aureus*) m.w. 17,600	20 mM sodium phosphate pH 7.0	DSC	25	1.45(0.04)	[50]
Ovalbumin (hen egg) m.w. $\sim$ 44,000	Water	DC	25	1.534(0.014)	[31]
Pepsinogen (porcine) m.w. 39,690	5 mM sodium phosphate 0.1 M NaCl pH 6.5–8.0	DSC	20	1.63(0.08)	[71]
Pepsin (porcine) m.w. 34,640		DSC	20	1.42(0.08)	[71]
Ribonuclease A (bovine pancrease) m.w. 13,690	20 mM glycine pH 4.0	DSC	5	1.42(0.04)	[62]
		DSC	25	1.52(0.04)	[62]
		DSC	50	1.64(0.04)	[62]
Ribonuclease T1 (*Aspergillus oryzae*) m.w. 11,070	10 mM glycine, Na-cacodylate, Na-borate, HEPES pH 7–10	DSC	5	1.32(0.06)	[72]
		DSC	25	1.45(0.06)	[72]
		DSC	50	1.61(0.06)	[72]
ROP (*Escherichia coli*) m.w. 6510	10 mM Na-phosphate	DSC	5	1.11(0.06)	[73]
	and 10 mM Na_2SO_4 pH 2–8	DSC	25	1.26(0.06)	[73]
		DSC	50	1.46(0.06)	[73]
WT	10 mM Na-phosphate, and 10 mM Na_2SO_4, pH 6.0	DSC	25	1.49_8	[74]
L41V variant			25	1.50_9	[74]
L41A variant			25	1.58_4	[74]
Streptokinase (*Streptoccocus equisimilis*) m.w. 47,000	10 mM Na-phosphate pH 7.5	DSC	25	1.42(0.17)	[75]
Tendamistat (*Streptomyces tendae*)	10 mM Na-phosphate and 10 mM Na_2SO_4 pH 2–8	DSC	5	1.44(0.07)	[76]
			25	1.52(0.07)	[76]
m.w. 7960			50	1.64(0.07)	[76]
			75	1.75(0.07)	[76]
α-Tropomyosin (rabbit muscle) m.w. 65,000	25 mM potassium phosphate 1 M KCl pH 7.1	DSC	25	1.30(0.08)	[77]
C-fragment (1–189) m.w. 22,000		DSC	25	1.40(0.08)	[77]
N-fragment (190–284) m.w. 43,400		DSC	25	1.80(0.08)	[77]
SH3 domain m.w. 6700	10 mM glycine or acetate pH 2–4	DSC	5	1.34(0.13)	[78]
			25	1.47(0.13)	[78]
			40	1.57(0.13)	[78]

Tryptophane synthase α-subunit (*Escherichia coli*) m.w. 28,609	1 mM borate 1 mM EDTA pH 7.3–8.9	DSC	20	1.80(0.08)	[79]
Ubiquitin (bovine) m.w. 8433	10 mM glycine or acetate pH 2–4	DSC	5	1.33(0.08)	[80]
		DSC	25	1.49(0.08)	[80]
		DSC	50	1.70(0.08)	[80]
Denatured state					
Adrenodoxin (bovine adrenal ferrodoxin) m.w. 14,020	40 mM glycine, 1 mM ascorbic acid, 10 mM mercaptoethanol, pH 8.5, holo form apo from 20 mM glycine or sodiumacetate pH 2.0–6.0	DSC	80	2.38(0.16)	[48]
			80	2.49(0.31)	[48]
Apocytochrome-C (horse heart) m.w. 11,700		DSC	5	1.83(0.04)	[62]
		DSC	25	2.03(0.04)	[62]
		DSC	50	2.15(0.04)	[62]
		DSC	75	2.22(0.04)	[62]
		DSC	100	2.23(0.04)	[62]
		DSC	125	2.25(0.04)	[62]
Apomyoglobin (sperm whale) m.w. 17,200	20 mM glycine pH 2.0	DSC	5	1.86(0.04)	[62]
		DSC	25	2.03(0.04)	[62]
		DSC	50	2.15(0.04)	[62]
		DSC	75	2.28(0.04)	[62]
		DSC	100	2.29(0.04)	[62]
		DSC	125	2.30(0.04)	[62]
Barnase (*Bacillus Amyloliquefaciens*) m.w. 12,365 irreversibly denatured	10 mM glycine or acetate pH 2–6	DSC	5	1.83(0.07)	[51]
		DSC	25	1.89(0.07)	[51]
		DSC	50	2.01(0.07)	[51]
		DSC	75	2.14(0.07)	[51]
		DSC	100	2.18(0.07)	[51]
		DSC	125	2.27(0.07)	[51]
Barstar (*Bacillus amyloliquefaciens)* m.w. 10,780		DSC	95	2.34(0.13)	[52]
		DSC	65	2.21(0.14)	[53]
BPTI (bovine pancrease) denatured by reducing and methylating all Cys residues m.w. 6655	10 mM glycine or acetate pH 2–4	DSC	5	1.89(0.07)	[54]
		DSC	25	2.03(0.07)	[54]
		DSC	50	2.12(0.07)	[54]
		DSC	75	2.16(0.07)	[54]
		DSC	100	2.18(0.07)	[54]
		DSC	125	2.16(0.07)	[54]
Collagen (pike skin) m.w. 93,000	20 mM glycine pH 3.0	DSC	25	1.55(0.04)	[50]
Cro repressor (λ phage) m.w. 14,700/dimer	10 mM acetate, pH 5.0	DSC	20	2.31(0.07)	[59]
		DSC	80	2.38(0.08)	[59]
Interleukin-1β (human) m.w. 17,381 irreversibly denatured	10 mM glycine or acetate pH 2–4	DSC	5	1.92(0.08)	[65]
		DSC	25	2.05(0.08)	[65]
		DSC	50	2.16(0.08)	[65]
		DSC	75	2.21(0.08)	[65]
		DSC	100	2.26(0.08)	[65]
		DSC	125	2.26(0.08)	[65]

Table 7 (continued)

Protein (source)	Solvent	Method	T°C	$C^0_{P,\phi}$	Reference
Lysozyme (hen egg) m.w. 14,670 denatured by reduction and carboxymethylation of all Cys residues	20 mM glycine pH 2.0–4.0	DSC	5	1.72(0.04)	[62]
		DSC	25	1.87(0.04)	[62]
		DSC	50	2.01(0.04)	[62]
		DSC	75	2.12(0.04)	[62]
		DSC	100	2.14(0.04)	[62]
		DSC	125	2.15(0.04)	[62]
Myoglobin (sperm whale) m.w. 17,760	20 mM glycine pH 2.0–3.0	DSC	25	1.98(0.04)	[50]
Nuclease (*Staphyloccocus aureus*) m.w. 17,600	20 mM glycine pH 2.0–3.0	DSC	25	1.90(0.06)	[50]
Ribonuclease A (bovine pancreas) m.w. 13,690 denatured by reduction and carboxymethylation of all Cys residues	20 mM glycine, pH 2.0–4.0	DSC	5	1.64(0.04)	[62]
		DSC	25	1.85(0.04)	[62]
		DSC	50	1.97(0.04)	[62]
		DSC	75	2.08(0.04)	[62]
		DSC	100	2.12(0.04)	[62]
		DSC	125	2.14(0.04)	[62]
Ribonuclease T1 (*Aspergillus oryzae*) m.w. 11,420 denatured by reduction and carboxymethylation of all Cys residues	10 mM glycine, Na-cacodylate, Na-borate, or HEPES pH 7–10	DSC	5	1.82(0.07)	[72]
		DSC	25	1.93(0.07)	[72]
		DSC	50	2.06(0.07)	[72]
		DSC	75	2.17(0.07)	[72]
		DSC	100	2.25(0.07)	[72]
		DSC	125	2.27(0.07)	[72]
ROP (*Escherichia coli*) m.w. 6510 WT	10 mM Na-phosphate, and 10 mM Na_2SO_4, pH 6.0	DSC	90	2.27_8	[74]
L41V variant			90	2.27_4	[74]
L41A variant			90	2.26_6	[74]
Streptokinase (*Streptoccocus equisimilis*) m.w. 47,236	10 mM Na-phosphate, pH 7.5	DSC	25	2.05(0.17)	[75]
Tryptophane synthase α-subunit (*Escherichia coli*) m.w. 28,609	1 mM borate, 1 mM EDTA, pH 7.3–8.9	DSC	20	2.22(0.08)	[79]
Ubiquitin (bovine) m.w. 8433 irreversibly denatured	10 mM glycine or acetate pH 2–4	DSC	5	2.01(0.08)	[80]
		DSC	25	2.17(0.08)	[80]
		DSC	50	2.30(0.08)	[80]
		DSC	75	2.35(0.08)	[80]
		DSC	100	2.40(0.08)	[80]
		DSC	125	2.40(0.08)	[80]

Table 8
Temperature dependence of the partial molar heat capacities (J K^{-1} mol^{-1}) the peptide unit (–CHCONH–) and of the side chains ($–R_i$) of amino acid residues for the temperature range 5–125°C [62]

	Temperature (°C)					
	5	25	50	75	100	125
–CHCONH–$–R_i$	3.7	15.2	26.2	29.8	33.7	33.7
Ala	175.7	166.7	156.2	144.7	134.6	124.1
Arg	204.6	273.4	305.8	315.1	318.7	318.5
Asn	72.9	88.8	109.8	125.2	140.5	154.2
Asp	72.8	89.0	106.2	124.5	140.7	154.3
Cys	225.4	237.6	250.8	260.7	268.2	276.1
Gln	168	180.2	193.4	203.3	210.8	218.7
Glu	168.3	179.0	192.0	203.7	211.4	217.8
Gly	82.3	78.0	71.7	66.4	59.7	53.9
His	205.7	179.6	177.2	179.6	187.1	196.8
Ile	406.8	402.3	397.1	390.8	386	380.8
Leu	385.9	381.7	377.8	372.9	369.4	365.5
Lys	215.1	249.8	266.9	274.4	278.1	274.4
Met	197.1	175.9	158.1	150.3	148.1	143.9
Phe	395.7	383.0	370.3	358.4	348.3	339.6
Pro	214.6	177.7	152.3	142.8	135.6	130.1
Ser	75.6	81.2	85.7	91.4	97.3	102.1
Thr	194.2	184.5	182.2	186.5	1990	216.2
Trp	471.2	458.5	445.8	433.9	423.8	415.1
Tyr	310.6	301.7	295.2	294.5	300.1	304.0
Val	324.6	314.4	305.0	294.7	285.7	269.6
Heme	875	1012	1155	1265	1375	1506

bility of determination of the partial molar heat capacity of proteins by using the NMR technique [82].

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