

4e. Heat Capacities

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In both Tables 4e-1 and 4e-2, temperatures are given in kelvins (K).¹ The formula weights accompanying the symbols of the elements are based on the International Atomic Weights of 1961 ($C^{12} = 12.0000$). The heat capacity is given in calories per kelvin per gram-formula-weight (1 cal = 4.1840 joules). Except for separate listings for allotropic modifications of a few elements, the heat capacity is given only for the physical state in which the element is stable at one atmosphere pressure and at the temperature in question. (For condensed gases of Table 4e-1, the values are given for the saturation pressures.) This state of the element (crystalline, liquid, or gaseous) is indicated in parentheses by the appropriate letters, except that when two or more crystalline forms of an element are known, these are distinguished as α , β , γ , etc. In Table 4e-1 the values given are for the crystalline phase unless indicated otherwise; changes in phase are identified. The asterisks (*) indicate that the values given are in the region of sharp transitions or "heat effects," and the parentheses enclose values that were obtained by extrapolation or interpolation over a broad temperature range. These values may contain large errors. No attempt was made to resolve the discrepancies in the existing data for the few elements where Tables 4e-1 and 4e-2 disagree at the temperature 298.15 K.

In the preparation of Table 4e-1, the results of an unpublished critical analysis of elemental substances being conducted as a part of the National Standard Reference Data System have largely been used. Wherever data more recent than the above analysis were known to have been published, they were examined for any major changes. When the authors tabulated smoothed values at even temperatures, their values were freely used with minor adjustments whenever needed. The following compilations were also used in the preparation of the table: K. K. Kelley, Contributions to the Data on Theoretical Metallurgy: XIV, Entropies of the Elements and Inorganic Compounds, *U.S. Bur. Mines Bull.* 592, 1961; and R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, "Selected Values of Thermodynamic Properties of Metals and Alloys," John Wiley & Sons, Inc., New York, 1963.

In Table 4e-2, the values cover, in general, only the temperature range of experimental measurements (or of statistical-thermodynamic calculation in the case of the

¹ The name of the unit of thermodynamic temperature was changed from degree Kelvin (symbol: °K) to kelvin (symbol: K); and kelvin is now defined as the fraction 1/273.16 of the thermodynamic temperature of the triple point of water [*NBS Tech. News Bull.* **52**, 10 (1968)]. The temperatures and temperature intervals used in the experimental measurements of heat capacity are taken to be consistent with the above definition within the accuracy of the values of heat capacity given in Table 4e-1 and 4e-2.

TABLE 4c-1. MOLAR HEAT CAPACITY AT CONSTANT PRESSURE OF ELEMENTAL SUBSTANCES AT LOW TEMPERATURES, CAL/MOLE·K
As revised December, 1967

Element	10	15	20	25	30	50	70	100	150	200	250	298.15
Aluminum Al 26.9815	0.0098	0.026	0.054	0.11	0.20	0.91	1.85	3.12	4.43	5.16	5.56	5.82
Antimony Sb 121.75	0.10	0.36	0.74	1.17	1.59	3.09	4.10	4.92	5.55	5.95	6.03	6.03
Argon A 39.948	0.90	1.89	2.82	3.70	4.39	5.95	6.96(c)	4.97(g)	4.97	4.97	4.97	4.97
Arsenic As 74.9216	(0.03)	0.12	0.27	0.50	0.78	1.90	2.88	3.98	4.94	5.13	5.75	5.89
Barium Ba 137.34	0.44	1.11	1.90	2.70	3.50	5.36	7.97	9.23	11.75	12.85	14.16(c)	(6.30)
Beryllium Be 9.0122	0.0006	0.002	0.003	0.006	0.009	0.04	0.12	0.43	1.36	2.41	3.30	3.93
Bismuth Bi 208.980	0.51	1.21	1.80	2.32	2.86	4.29	4.99	5.52	5.85	5.99	6.11	6.19
Boron (crystalline) B 10.811	0.006	0.009	0.02	0.04	0.12	0.26	0.77	1.45	2.11	2.65
Boron (amorphous) B 10.811	0.02	0.01	0.01	0.04	0.12	0.33	0.86	1.55	2.22	2.86
Bromine Br 159.88	(0.55)	1.72	3.04	4.30	5.36	7.97	9.23	10.42	11.75	12.85	14.16	18.08(0)
Cadmium Cd 112.40	0.22	0.69	1.23	1.79	2.30	3.80	4.54	5.28	5.74	5.94	6.08	6.22
Calcium Ca 40.08	0.05	0.15	0.35	0.62	0.97	2.60	3.64	4.66	5.49	5.91	(6.12)	(6.30)
Carbon (graphite) C 12.01115	0.004	0.01	0.02	0.03	0.04	0.12	0.23	0.40	0.77	1.18	1.63	2.04
Carbon (diamond) C 12.01115	0.0001	0.0002	0.0003	0.0007	0.001	0.005	0.016	0.059	0.24	0.56	0.99	1.46
Carbon C 140.12	1.05*	1.14*	1.76	2.46	3.08	3.19	5.83	6.46	6.71*	(6.90)	6.94	(6.44)
Cesium Cs 132.905	2.64	3.91	4.67	5.08	5.36	5.80	5.97	6.16	6.41*	6.59*	7.67*	7.67*
Chlorine Cl 37.906	(0.30)	0.89	1.85	2.89	3.99	6.93	8.68	10.10	12.20(c)	15.95(0)	15.95(0)	8.11(g)
Chromium Cr 51.996	0.006	0.014	0.026	0.054	0.095	0.45	1.20	2.39	3.94	4.81	5.30	5.56
Cobalt Co 58.9332	0.014	0.037	0.071	0.14	0.24	0.98	2.05	3.34	4.65	5.33	5.75	5.95
Copper Cu 63.54	0.013	0.044	0.110	0.230	0.405	1.47	2.60	3.82	4.90	5.41	5.68	5.84
Dysprosium Dy 162.50	(0.18)	0.60	1.34	2.20	3.04	5.52	6.97*	8.32*	10.88*	12.90	13.90	14.48
Erbium Er 167.26	(0.47)	1.60	5.02*	3.73	4.60	6.78*	7.35*	8.57	10.21	11.46	12.59	13.72
Europium Eu 151.96	0.93	2.08	2.38	3.31	3.31	6.03(c)	11.79(c2)	13.56(l)	16.99	7.10	7.28	7.49
Fluorine F ₂ 37.9968	0.18	1.76	3.10	4.61	6.77	2.44	4.64	5.40	6.91	7.81	8.64	9.95*
Gadolinium Gd 157.25	0.058	0.46	1.06	1.77	2.44	4.19	5.47	6.43	7.27	8.26	9.55	10.24
Gallium Ga 69.72	0.058	0.25	0.54	0.84	1.19	2.45	3.47	4.30	5.30	5.44	5.03	5.37
Germanium Ge 72.59	0.014	0.077	0.22	0.41	0.63	1.18	2.27	3.30	4.38	5.64	5.84	6.08
Gold Au 196.967	0.103	0.352	0.762	1.25	1.76	3.41	4.38	5.12	6.01	6.15	6.47	6.73
Hafnium Hf 178.49	0.04	0.16	0.41	0.77	1.26	2.60	4.00	4.92	5.55	5.83	6.01	6.15
Helium He 4.0026	4.97(g)	4.97	4.97	4.97	4.97	4.97	4.97	4.97	4.97	4.97	4.97	4.97
Holmium Ho 161.930	0.64	1.57*	2.29*	3.67	5.86	7.41	9.39	11.34	12.33	13.42	14.49	15.49
n-Hydrogen H ₂ 2.01594	0.47(c)	3.32(l)	4.55	6.22	10.16(l)	4.88(g)	5.06	5.39	6.07	6.52	6.77	6.89
n-Deuterium D ₂ 4.02820	0.54(c)	1.64(c)	5.49(l)	5.00(g)	5.95	6.89	7.19	7.03	6.98	6.98	6.98	6.98
Inidium In 114.82	< 0.43	0.43	1.01	1.67	2.36	2.9	4.41	5.08	5.58	5.99	6.17	6.31
Iodine I ₂ 253.8088	0.96	2.45	3.87	5.14	6.16	8.57	9.96	10.96	11.86	12.32	12.73	13.01
Iridium Ir 192.2	(0.014)	0.038	0.094	0.22	0.43	1.75	2.98	4.15	5.17	5.58	5.87	(6.12)
Iron Fe 55.847	0.017	0.034	0.061	0.11	0.18	0.73	1.61	2.88	4.33	5.13	5.63	5.99
Krypton Kr 83.80	1.46	2.90	3.67	4.43	5.0	6.01	6.57	7.55(c)	9.97(g)	4.97	4.97	4.97
Lanthanum La 138.91	0.26	0.80	1.48	2.20	2.8	4.41	5.12	5.64	6.04	6.17	6.27	6.65
Lead Pb 207.19	0.66	1.68	2.58	3.37	3.91	5.12	5.57	5.85	6.04	6.15	6.26	6.36
Lithium Li 6.939	0.015	0.043	0.095	0.17	0.23	0.97	1.86	3.19*	4.48*	5.60	5.91	5.91
Lutetium Lu 174.97	0.12	0.40	0.88	1.46	2.02	3.79	4.72	5.40	6.16	6.31	6.42	6.42
Magnesium Mg 24.312	0.010	0.034	0.086	0.18	0.33	2.51	3.77	4.90	5.43	5.75	5.95	5.95
Manganese (c) Mn 54.9380	0.04	0.068	0.12	0.19	0.33	2.24	3.52*	4.74	5.75	6.51	6.77	6.97

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Mercury Hg 200.59	1.12	1.85	2.52	3.04	3.53	4.76	5.36	5.80	6.19	6.52(c)	6.78(1)
Molybdenum Mo 95.94	0.010	0.024	0.050	0.099	0.13	0.90	1.92	3.21	4.52	5.50	5.68
Neodymium Nd 144.24	1.26	1.79	2.45*	2.85	3.39	5.16	(5.99)	(6.36)	(6.77)	(6.97)	(6.57)
Neon Ne 20.183	1.25	2.85	4.37(0)	8.44(1)	4.97(g)	4.97	4.97	4.97
Neptunium Np (237)	0.024	0.043	0.077	0.14	0.23	0.96	1.97	3.28	4.62	5.37	5.83
Nickel Ni 58.71	0.050	0.12	0.24	0.42	0.65	1.88	3.02	4.17	5.10	5.52	5.77
Niobium (columbium) Nb(Cb) 92.906	1.06	2.87	4.50	6.50	8.26(c ₁)	9.92(c ₂)	13.4(1)	6.96(E)	6.96	6.96	6.96
Nitrogen N ₂ 28.0134	(5.90)
Osmium Os 190.2	0.60	1.59	3.27(e ₁)	5.30(c ₂)	11.0(c ₃)	12.7(0)	1.96	6.96	6.96	6.98	6.98
Oxygen O ₂ 31.9988	0.050	0.12	0.24	0.41	0.67	1.96	1.10	1.96	5.30	5.79	6.06
Palladium Pd 106.4	0.06	0.17	0.36	0.65	1.03	2.56	3.68	4.65	5.17	5.83	6.05
Phosphorus (red) P 30.9738	5.50*	5.50*	5.34*	6.19
Phosphorus (white) P 30.9738	7.65*
Platinum Pt 195.09	(6.30)
Plutonium Pu (239)
Polonium Po (210)	0.66	1.51	2.34	3.08	3.70	5.01	5.52	6.22	6.44	6.70	7.06
Potassium K 39.1022	0.99	2.02	3.18	4.36	5.77	6.18*	6.30*	6.42	6.51	(6.56)	(6.59)
Praseodymium Pr 140.907	0.016	0.033	0.067	0.15	0.32	0.54	1.89	3.08	4.31	5.33	6.14
Rhenium Re 186.2	0.16	0.33	0.67	1.14	0.26	1.20	2.32	3.61	4.82	5.75	5.97
Rhodium Rh 102.905	0.73	2.95	3.83	4.49	4.10	5.60	5.88	6.10	6.34	6.56	7.39
Rubidium Rb 85.47	0.022	0.042	0.084	0.17	0.39	0.89	0.92	3.23	4.52	5.17	5.80
Ruthenium Ru 101.07	0.010	0.022	0.052	0.177	0.40	3.11	5.39	7.01	8.28	8.47	7.06
Samarium Sm 150.35	0.63*	1.35*	2.04	3.20	5.54	7.70	9.08*	9.92	10.55	11.59	12.12
Scandium Sc 44.956	0.038	0.087	0.17	0.29	0.77	1.51	2.62	3.42	4.34	5.18	5.80
Selenium Se 78.96	0.18	0.45	0.83	1.29	2.17	3.53	4.02	4.74	5.86	6.74	7.36
Silicon Si 28.086	0.0018	0.0073	0.0023	0.057	0.12	0.53	1.74	2.86	3.74	4.77	5.95
Silver Ag 107.870	0.041	0.160	0.394	0.733	1.14	2.79	4.80	5.47	6.77	6.45	6.06
Sodium Na 22.9898	0.14	0.42	0.88	1.44	2.00	3.70	4.65	5.36	5.91	6.20	6.74
Strontium Sr 87.62	0.17	0.57	1.14	1.88	2.00	3.70	4.65	5.36	5.91	6.30	6.30
Sulfur (monoclinic) S 32.064	0.10	0.31	(0.61)	(0.61)	(0.86)	(1.08)	1.77	2.36	3.10	4.80	5.29
Sulfur (rhombic) S 32.064	0.10	0.31	0.61	0.86	1.00	2.60	3.75	4.74	5.45	5.76	5.42
Tantalum Ta 180.948	0.050	0.15	0.34	0.62	1.00	2.60	3.75	4.74	5.45	5.94	6.05
Technetium Tc (99)	(5.80)
Tellurium Te 127.60	0.21	0.62	1.09	1.85	2.64	5.10	5.46	7.56	8.90	11.20	7.55
Terbium Tb 158.924	0.47	1.07	1.85	3.18	3.80	5.01	5.60	5.48	6.06	6.15	6.23
Thallium Tl 204.37	0.81	1.59	2.40	3.11	4.40	4.05	4.88	5.48	5.97	6.22	6.53
Thorium Th 232.038	0.16	0.52	1.11	2.54	3.93*	5.27*	9.12*	8.84*	6.04*	6.20*	6.39*
Thulium Tm 168.334	0.47	1.32	2.54	3.93*	5.89	1.58	2.69	3.70	4.67	5.44	6.16
Tin (gray) Sn 118.69	0.16	0.50	0.89	1.24	1.65	2.20	3.68	4.53	5.35	5.81	6.02
Tin (white) 118.69	0.22	0.64	1.11	1.65	2.27	1.13	2.17	3.43	4.68	5.32	5.97
Titanium Ti 47.90	0.015	0.036	0.079	0.15	0.27	0.50	0.88	1.80	2.57	3.83	5.66
Tungsten W 183.80	0.011	0.032	0.077	0.17	0.32	1.39	2.17	3.75	5.32	4.90	6.40
Uranium U 238.03	0.084	0.31	0.73	1.31	1.93	3.75	4.59	5.87	6.17	6.40	6.61
Vanadium V 50.942	0.028	0.052	0.087	0.13	0.23	0.89	1.83	3.07	4.41	5.16	5.97
Xenon Xe 131.30	1.94	3.24	4.00	4.73	5.19	5.99	6.32	6.75	8.04(c)	4.97	4.97
Ytterbium Yb 173.04	0.35	1.05	1.89	2.70	3.34	4.78	5.74	6.00	6.14	6.25	6.39
Yttrium Y 88.905	0.055	0.19	0.45	0.70	1.26	2.91	4.02	4.95	5.64	6.00	6.34
Zinc Zn 65.37	0.17	0.42	0.77	1.16	2.65	3.67	4.61	5.43	5.74	5.94	6.07
Zirconium Zr 91.22	0.03	0.10	0.25	0.45	0.75	2.18	3.37	5.74	5.30	5.74	6.08

TABLE 4e-2. MOLAR HEAT CAPACITY AT CONSTANT PRESSURE OF THE CHEMICAL ELEMENTS
AT HIGHER THAN ROOM TEMPERATURE, CAL/MOLE · K
As revised December, 1967

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Manganese Mn 54.9380.....	6.76	7.21	7.63	8.01	8.35(α)	9.01(β)	9.21(β)	10.99(δ)	5.039(g)	5.252(g)
Mercury Hg 200.59.....	6.54	6.48	6.48(1)	4.968(κ)	4.968	4.968	4.968	4.968	4.968	4.968
Molybdenum Mo 95.94.....	6.05	6.25	6.38	6.48	6.55	6.70	6.93	7.47	8.53	10.46(c)
Neodymium Nd 144.24.....	5.73(c)	5.55(α)	6.88	7.24	7.66	8.14	8.71	10.65(γ)	4.968	4.968
Neon Ne 20.183.....	4.968(κ)	4.968	4.968	4.968	4.968	4.968	4.968	4.968	4.968	4.968
Nickel Ni 58.71.....	6.23(c)	6.80	7.37	8.31	7.37	7.44	7.88	8.34	8.65(c)	10.30(l)
Nichium (columbium) Nb(Cb) 92.906.....	5.88(c)	6.09	6.18	6.28	6.38	6.48	6.68	6.88(κ)	8.33	8.60
Nitrogen N ₂ 28.0134.....	6.96(g)	6.99	7.07	7.20	7.35	7.51	7.82	8.06	8.33	8.76
Osmium Os 190.2.....	5.90(c)	5.99	6.09	6.18	6.27	6.63	6.54	6.72	7.00(c)	9.03(g)
Oxygen O ₂ 31.9988.....	7.02(κ)	7.20	7.43	7.67	7.88	8.06	8.34	8.53	8.74	9.03(g)
Ozone O ₃ 47.9982.....	9.38(κ)	10.46	11.30	11.92	12.37	12.70	13.15	13.43	13.68(g)	13.68(g)
Palladium Pd 106.4.....	6.21(c)	6.35	5.49	6.62	6.76	6.90	7.17	7.44	7.86(c)	7.86(c)
Phosphorus (red, trichloride) P 30.9738.....	5.07(c)	5.51	5.85	6.16	6.50(c)	7.08	7.34	7.72	8.37(c)	8.37(c)
Phosphorus (white) P 30.9738.....	5.70(β)	6.29(1)	5.29(1)	6.57	6.70	6.82	7.08	7.34	7.72	8.37(c)
Platinum Pt 195.09.....	6.18(c)	6.31	6.44	7.00(6)	9.00(6)	8.40(κ)	7.11	7.26(κ)	4.968	4.968
Plutonium Pu(1239).....	7.64(α)	8.03(β)	8.53(γ)	7.34	7.20	7.13	7.11	7.26(κ)	4.968	4.968
Potassium K 39.102.....	0.70(c)	7.53(1)	7.34	7.20	7.13	7.26(κ)	7.11	7.26(κ)	4.968	4.968
Radon Rn [222].....	4.968(κ)	4.968	4.968	4.968	4.968	4.968	4.968	4.968	4.968	4.968
Rhenium Re 186.2.....	6.16(c)	6.22	6.32	6.43	6.56	6.69	6.69	7.22(κ)	7.22(κ)	7.22(κ)
Rhodium Rh 102.905.....	5.97(c)	6.21	6.45	6.69	6.93	7.17	7.17	7.24(c)	7.24(c)	7.24(c)
Ruthenium Ru 101.07.....	5.75(c)	5.82	5.91	6.04	6.23	6.42	6.75	7.11	7.24(c)	7.24(c)
Samarium Sm 150.35.....	7.06(α)	7.93	8.94	9.75	10.19	10.52	10.82(α)	11.22(β)	11.22(β)	11.22(β)
Scandium Sc 44.956.....	6.10(c)	6.29	6.41	6.57	6.75	6.96	7.46	8.06	9.14(α)	9.14(α)
Selenium (metallic) Se 78.96.....	6.06(c)	6.65(c)	8.40(l)	8.40(l)	8.40(l)	8.40(l)	8.40(l)	8.40(l)	8.40(l)	8.40(l)
Silicon Si 28.086.....	4.78(c)	5.30	5.61	5.82	5.99	6.13	6.35	6.49	6.66(c)	6.66(c)
Silver Ag 107.870.....	6.07(c)	6.18	6.30	6.42	6.56	6.72	7.15	7.62(c)	7.62(c)	7.62(c)
Sodium Na 22.9898.....	0.72(c)	7.53(1)	7.93	7.12	7.00	6.92	6.92(l)	6.92(l)	6.92(l)	6.92(l)
Sulfur S 32.064.....	5.40(rh)	7.73(1)	9.08	8.20	7.80(l)	6.39	6.45	6.57	6.69	6.87
Tantalum Ta 180.948.....	5.06(c)	6.22	6.30	6.33	6.39	6.45	6.57	6.69	6.87	7.17
Tellurium Te 127.60.....	5.14(c)	6.68	7.21	7.73	8.26(c)	9.00(l)	9.00(l)	9.00(l)	9.43(c)	9.46(r)
Thallium Tl 204.37.....	5.29(α)	6.57	7.03(α)	7.2(1)	7.45	7.76	8.06	8.67	9.23(α)	9.23(α)
Thorium Th 232.038.....	5.53(α)	6.85	7.15	7.45	7.45	7.76	7.08	7.52	7.89	7.89
Thulium Tm 168.934.....	5.46(c)	6.49	6.51	6.59	6.76	6.85	6.85(l)	7.10(β)	7.85(β)	7.85(β)
Tin (white) Sn 118.69.....	5.45(c)	6.89	7.32(c)	6.87(l)	6.85	6.85(l)	7.25	7.25	7.14	7.14
Titanium Ti 47.90.....	5.98(α)	6.31	6.53	6.77	7.01	7.01	6.37	6.59	6.80	6.80
Tungsten (wolfram) W 183.85.....	5.81(c)	5.96	6.06	6.16	6.27	6.27	6.27	6.37	6.45(l)	6.45(l)
Uranium U 238.03.....	6.61(α)	7.10	7.65	8.31	9.08	9.99(κ)	10.26(β)	9.15(γ)	8.69(c)	8.69(c)
Vanadium V 50.934.....	5.95(c)	6.27	6.44	6.57	6.70	6.85	7.27	7.85	8.69(c)	8.69(c)
Xenon Xe 130.30.....	4.968(g)	4.968	4.968	4.968	4.968	4.968	4.968	4.968	4.968	4.968
Ytterbium Yb 173.04.....	6.39(α)	6.60	7.41	7.13	7.25	7.37	7.64(α)	8.79(l)	4.97(E)	4.97
Yttrium Y 8.905.....	6.34(α)	6.49	6.65	6.82	7.00	7.18	7.53	7.90	8.43(α)	8.43(α)
Zinc Zn 65.37.....	6.07(c)	6.31	6.55	6.78	7.5(l)	7.5(l)	7.5(l)	7.5(l)	4.968	4.968
Zirconium Zr 91.22.....	6.06(α)	6.54	6.78	7.01	7.23	7.45	7.90(α)	7.50(β)	7.50(β)	7.50(β)

gases). With the exception of B (amorphous), C (diamond), Se, Te, and the gases H₂, D₂, Eu, Sm, Tm, and Yb, the tabulated values are based on (1) R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, "Selected Values of Thermodynamic Properties of Metals and Alloys," John Wiley & Sons, Inc., New York, 1963 (and later looseleaf supplements); (2) JANAF Thermochemical Tables, Clearinghouse, U.S. Department of Commerce, Springfield, Va. (*PB Rept. 168370*, 1965; *PB Rept. 168-370-1*, 1966) (and later looseleaf supplements); and (3) J. Hilsenrath, C. G. Messina, and W. H. Evans, Ideal Gas Thermodynamic Functions for 73 Atoms and Their First and Second Ions to 10,000 K, *Air Force Weapons Lab. Rept. TDR-64-44*, Kirtland Air Force Base, N.Mex., 1964.

TABLE 4e-3. HEAT CAPACITY OF WATER
(Osborne, Stimson, and Ginnings, National Bureau of Standards)

Temp., °C	$\frac{J}{g \cdot K}$	Temp., °C	$\frac{J}{g \cdot K}$
0	4.2177	50	4.1807
5	4.2022	55	4.1824
10	4.1922	60	4.1844
15	4.1858	65	4.1808
20	4.1819	70	4.1896
25	4.1796	75	4.1928
30	4.1785	80	4.1964
35	4.1782	85	4.2005
40	4.1786	90	4.2051
45	4.1795	95	4.2103
50	4.1807	100	4.2160

As a first approximation in explaining the temperature dependence of the heat capacity of solids, Einstein made the assumption that all oscillators in the lattice vibrated with the same frequency ν_0 . If h is Planck's constant and k is Boltzmann's constant, let

$$\Theta_E = \frac{h\nu_0}{k} \quad x = \frac{\Theta_E}{T}$$

and denote the zero-point energy per mole by U_0 . Then the Einstein theory of specific heat yields for the molar energy U at the temperature T

$$(Einstein) \frac{U - U_0}{3RT} = \frac{x}{e^x - 1} \quad (4e-1)$$

where R is the universal gas constant. The Einstein molar heat capacity at constant volume is given by $C_V = dU/dT$, or

$$(Einstein) \frac{C_V}{3R} = \frac{x^2 e^x}{(e^x - 1)^2} \quad (4e-2)$$

The molar entropy S is equal to $\int(C_V/T) dT$, whence

$$(Einstein) \frac{S}{3R} = \frac{x}{e^x - 1} - \ln(1 - e^{-x}) \quad (4e-3)$$

Numerical values of the quantities in Eqs. (4e-1), (4e-2), and (4e-3) are given in Tables 4e-4, 4e-5 and 4e-6, taken from "Contributions to the Thermodynamic Functions by a Planck-Einstein Oscillator in One Degree of Freedom," prepared by Herrick L. Johnston, Lydia Savedoff, and Jack Belzer, of the Cryogenic Laboratory of the

TABLE 4e-4. $\frac{U - U_0}{3RT}$ (EINSTEIN)

$\frac{\Theta_E}{T}$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	1.00000	0.95083	0.90333	0.85749	0.81330	0.77075	0.72982	0.69050	0.65277	0.61661
1	0.58198	0.54886	0.51722	0.48702	0.45824	0.43083	0.40475	0.37998	0.35646	0.33416
2	0.31304	0.29304	0.27414	0.25629	0.23945	0.22356	0.20861	0.19453	0.18129	0.16886
3	0.15719	0.14624	0.13598	0.12638	0.11739	0.10898	0.10113	0.09380	0.08695	0.08057
4	0.07463	0.06909	0.06394	0.05915	0.05469	0.05055	0.04671	0.04314	0.03983	0.03676
5	0.03392	0.03128	0.02885	0.02658	0.02450	0.02257	0.02079	0.01914	0.01761	0.01621
6	0.01491	0.01371	0.01261	0.01159	0.01065	0.00979	0.00899	0.00826	0.00758	0.00696
7	0.00639	0.00586	0.00538	0.00494	0.00453	0.00415	0.00381	0.00349	0.00320	0.00293
8	0.00269	0.00246	0.00225	0.00206	0.00189	0.00173	0.00158	0.00145	0.00133	0.00121
9	0.00111	0.00102	0.00093	0.00085	0.00078	0.00071	0.00065	0.00059	0.00054	0.00050
10	0.00045	0.00042	0.00038	0.00035	0.00032	0.00029	0.00026	0.00024	0.00022	0.00020
11	0.00018	0.00017	0.00015	0.00014	0.00013	0.00012	0.00011	0.00010	0.00009	0.00008
12	0.00007	0.00007	0.00006	0.00006	0.00005	0.00005	0.00004	0.00004	0.00004	0.00003
13	0.00003	0.00003	0.00002	0.00002	0.00002	0.00002	0.00002	0.00002	0.00001	0.00001
14	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001

TABLE 4e-5. $\frac{C_v}{3R}$ (EINSTEIN)

$\frac{\Theta_E}{T}$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	1.00000	0.99917	0.99667	0.99253	0.98077	0.97942	0.97053	0.96015	0.94833	0.93515
1	0.92067	0.90499	0.88817	0.87031	0.85151	0.83185	0.81143	0.79035	0.76869	0.74657
2	0.72406	0.70127	0.67827	0.65515	0.63200	0.60889	0.58589	0.56307	0.54049	0.51820
3	0.49627	0.47473	0.45363	0.43301	0.41289	0.39331	0.37420	0.35584	0.33799	0.32073
4	0.30409	0.28806	0.27264	0.25783	0.24363	0.23004	0.21704	0.20462	0.19277	0.18149
5	0.17074	0.16053	0.15083	0.14162	0.13290	0.12464	0.11683	0.10944	0.10247	0.09588
6	0.08968	0.08383	0.07833	0.07315	0.06828	0.06371	0.05942	0.05539	0.05162	0.04808
7	0.04476	0.04166	0.03876	0.03605	0.03351	0.03115	0.02894	0.02687	0.02495	0.02316
8	0.02148	0.01993	0.01848	0.01713	0.01587	0.01471	0.01362	0.01261	0.01168	0.01081
9	0.01000	0.00925	0.00855	0.00791	0.00731	0.00676	0.00624	0.00577	0.00533	0.00492
10	0.00454	0.00419	0.00387	0.00357	0.00329	0.00304	0.00280	0.00258	0.00238	0.00219
11	0.00202	0.00186	0.00172	0.00158	0.00145	0.00134	0.00123	0.00114	0.00104	0.00096
12	0.00088	0.00081	0.00075	0.00069	0.00063	0.00058	0.00054	0.00049	0.00045	0.00042
13	0.00038	0.00035	0.00032	0.00030	0.00027	0.00025	0.00023	0.00021	0.00019	0.00018
14	0.00016	0.00015	0.00014	0.00013	0.00012	0.00011	0.00010	0.00009	0.00008	0.00008

Ohio State University, under contract between the Office of Naval Research and the Ohio State University Research Foundation, 1949.

Debye assumed that the oscillators occupying the lattice points in a crystalline solid vibrated with a continuous spectrum of frequencies from zero to a maximum value ν_m . Defining the "Debye temperature" Θ_D and y by the equations

$$\Theta_D = \frac{h\nu_m}{k} \quad y = \frac{\Theta_D}{T}$$

TABLE 4e-6. $\frac{S}{3R}$ (EINSTEIN)

$\frac{\Theta_E}{T}$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	∞	3.30300	2.61110	2.20772	1.92293	1.70350	1.52569	1.37684	1.24939	1.13845
1	1.04066	0.95363	0.87560	0.80521	0.74139	0.68331	0.63027	0.58171	0.53714	0.49617
2	0.45845	0.42367	0.39158	0.36194	0.33455	0.30921	0.28579	0.26410	0.24403	0.22546
3	0.20826	0.19234	0.17760	0.16396	0.15133	0.13964	0.12884	0.11883	0.10958	0.10102
4	0.09312	0.08580	0.07905	0.07281	0.06704	0.06172	0.05681	0.05228	0.04809	0.04423
5	0.04068	0.03740	0.03438	0.03159	0.02903	0.02666	0.02450	0.02249	0.02064	0.01896
6	0.01739	0.01596	0.01464	0.01343	0.01232	0.01130	0.01035	0.00949	0.00869	0.00797
7	0.00730	0.00660	0.00613	0.00562	0.00514	0.00470	0.00431	0.00394	0.00361	0.00330
8	0.00303	0.00276	0.00252	0.00231	0.00211	0.00193	0.00176	0.00162	0.00148	0.00135
9	0.00123	0.00113	0.00103	0.00094	0.00086	0.00078	0.00072	0.00065	0.00060	0.00055
10	0.00050	0.00046	0.00042	0.00038	0.00035	0.00032	0.00028	0.00026	0.00024	0.00022
11	0.00020	0.00019	0.00016	0.00015	0.00014	0.00013	0.00012	0.00011	0.00010	0.00009
12	0.00008	0.00008	0.00007	0.00006	0.00005	0.00005	0.00004	0.00004	0.00004	0.00003
13	0.00003	0.00003	0.00002	0.00002	0.00002	0.00002	0.00002	0.00002	0.00001	0.00001
14	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001

TABLE 4e-7. $\frac{U - U_0}{3RT}$ (DEBYE)

$\frac{\Theta_D}{T}$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	1.000000	.963000	.926999	.891995	.857985	.824963	.792923	.761858	.781759	.702615
1	.674416	.647148	.620798	.595351	.570793	.547107	.524275	.502280	.481103	.460726
2	.441128	.422291	.404194	.386816	.370137	.354136	.338793	.324086	.309995	.296500
3	.283580	.271215	.259385	.248070	.237252	.226911	.217029	.207589	.198571	.189959
4	.181737	.173888	.166396	.159246	.152424	.145914	.139704	.133780	.128129	.122739
5	.117597	.112694	.108016	.103555	.099300	.095241	.091369	.087675	.084152	.080789
6	.077581	.074520	.071598	.068809	.066146	.063604	.061177	.058858	.056644	.054528
7	.052506	.050573	.048726	.046960	.045271	.043655	.042109	.040630	.039214	.037858
8	.036560	.035317	.034126	.032984	.031890	.030840	.029834	.028869	.027942	.027053
9	.026200	.025380	.024593	.023837	.023110	.022411	.021739	.021092	.020470	.019872
10	.019296	.018741	.018207	.017692	.017196	.016718	.016257	.015812	.015384	.014970
11	.014570	.014185	.013813	.013453	.013106	.012770	.012445	.012131	.011828	.011534
12	.011250	.010975	.010709	.010452	.010202	.009960	.009726	.009499	.009279	.009066
13	.008859	.008658	.008463	.008275	.008091	.007913	.007740	.007572	.007409	.007251
14	.007097	.006947	.006801	.006660	.006522	.006388	.006258	.006132	.006008	.005888

$\frac{\Theta_D}{T}$	0	1	2	3	4	5	6	7	8	9
10	.019296	.014570	.011250	.008859	.007097	.005771	.004756	.003965	.003340	.002840
20	.002435	.002104	.001830	.001601	.001409	.001247	.001108	.000990	.000887	.000799
30	.000722	.000654	.000595	.000542	.000496	.000454	.000418	.000385	.000355	.000328
40	.000304	.000283	.000263	.000245	.000229	.000214	.000200	.000188	.000176	.000166

TABLE 4e-8. $\frac{C_V}{3R}$ (DEBYE)

$\frac{\Theta_D}{T}$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	1.000000	.999500	.998003	.915514	.992046	.987611	.982229	.975922	.968717	.960643
1	.951732	.942020	.931545	.920346	.908467	.895950	.882842	.869186	.855031	.840422
2	.825408	.810034	.794347	.778392	.762213	.745853	.729355	.712759	.696103	.679424
3	.662758	.646137	.629593	.613154	.596848	.580700	.564732	.548966	.533421	.518113
4	.503059	.488272	.473763	.459543	.445620	.432002	.418693	.405700	.393024	.380669
5	.368635	.356922	.345529	.334456	.323698	.313255	.303121	.293293	.283767	.274536
6	.265597	.256943	.248568	.240466	.232631	.225056	.217735	.210662	.203828	.197229
7	.190856	.184704	.178766	.173035	.167505	.162169	.157021	.152055	.147264	.142644
8	.138187	.133889	.129744	.125746	.121890	.118172	.114585	.111126	.107790	.104572
9	.101467	.098472	.095583	.092795	.090105	.087509	.085004	.082585	.080251	.077997
10	.075821	.073719	.071690	.069729	.067835	.066005	.064236	.062526	.060874	.059276
11	.057731	.056237	.054791	.053393	.052039	.050730	.049462	.048235	.047046	.045895
12	.044780	.043700	.042653	.041639	.040655	.039702	.038777	.037880	.037010	.036166
13	.035347	.034552	.033781	.033031	.032304	.031597	.030910	.030243	.029595	.028964
14	.028352	.027756	.027177	.026613	.026065	.025532	.025013	.024508	.024016	.023537
$\frac{\Theta_D}{T}$	0	1	2	3	4	5	6	7	8	9
10	.075821	.057731	.044780	.035347	.028352	.023071	.019018	.015859	.013361	.011361
20	.009741	.008414	.007318	.006405	.005637	.004987	.004434	.003959	.003550	.003195
30	.002886	.002616	.002378	.002168	.001983	.001818	.001670	.001538	.001420	.001314
40	.001218	.001131	.001052	.000980	.000915	.000855	.000801	.000751	.000705	.000662

the values of molar energy, molar heat capacity at constant volume and molar entropy were found to be

$$(Debye) \frac{U - U_0}{3RT} = D(y) = \frac{3}{y^2} \int_0^y \frac{z^3 dz}{e^z - 1} \quad (4e-4)$$

$$(Debye) \frac{C_V}{3R} = 4D(y) - \frac{3y}{e^y - 1} \quad (4e-5)$$

$$(Debye) \frac{S}{3R} = \frac{4}{3} D(y) - \ln(1 - e^{-y}) \quad (4e-6)$$

Values of the quantities in Eqs. (4e-4), (4e-5) and (4e-6) are given in Tables 4e-7, 4e-8 and 4e-9, prepared by John E. Kilpatrick and Robert H. Sherman, of the Los Alamos Scientific Laboratory, under contract with the U.S. Atomic Energy Commission, 1964.

To calculate $U - U_0$ in joules/mole, and C_V and S in joules/mole kelvin, take as the value of R

$$R = 8.3143 \text{ joules/mole kelvin}$$

To convert to calories, it must be kept in mind that there are three different calories:

The 15-degree calorie = 4.1858 joules

The International steam table calorie = 4.1868 joules

The thermochemical calorie = 4.1840 joules

TABLE 4e-9. $\frac{S}{3R}$ (DEBYE)

$\frac{\Theta_D}{T}$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	∞	3.636168	2.943771	2.539553	2.253613	2.032703	1.853102	1.702152	1.572296	1.458656
1	1.357896	1.267635	1.186113	1.111987	1.044212	0.981958	0.924550	0.871435	0.822152	0.776313
2	0.733585	0.693684	0.656362	0.621403	0.588010	0.557832	0.528900	0.501085	0.476064	0.451928
3	0.429176	0.407715	0.387463	0.368341	0.350279	0.333211	0.317077	0.301819	0.287386	0.273728
4	0.260801	0.248562	0.236970	0.225990	0.215585	0.205724	0.196375	0.187510	0.179103	0.171126
5	0.163557	0.156373	0.149554	0.143077	0.136926	0.131083	0.125530	0.120252	0.115234	0.110462
6	0.105924	0.101605	0.097495	0.093583	0.089858	0.086310	0.082930	0.079709	0.076639	0.073712
7	0.070920	0.068257	0.065715	0.063289	0.060972	0.058760	0.056646	0.054626	0.052695	0.050849
8	0.049083	0.047393	0.045775	0.044227	0.042744	0.041324	0.039963	0.038658	0.037407	0.036208
9	0.035057	0.033952	0.032892	0.031873	0.030895	0.029956	0.029053	0.028184	0.027349	0.026546
10	0.025773	0.025029	0.024313	0.023623	0.022959	0.022318	0.021701	0.021106	0.020532	0.019978
11	0.019444	0.018928	0.018431	0.017950	0.017485	0.017037	0.016603	0.016184	0.015778	0.015386
12	0.015007	0.014639	0.014284	0.013940	0.013607	0.013284	0.012972	0.012669	0.012375	0.012090
13	0.011814	0.011546	0.011286	0.011034	0.010790	0.010552	0.010321	0.010097	0.009880	0.009669
14	0.009463	0.009263	0.009069	0.008881	0.008697	0.008519	0.008345	0.008176	0.008011	0.007851
$\frac{\Theta_D}{T}$	0	1	2	3	4	5	6	7	8	9
10	0.025773	0.019444	0.015007	0.011814	0.009463	0.007695	0.006341	0.005287	0.004454	0.003787
20	0.003247	0.002805	0.002439	0.002135	0.001879	0.001662	0.001478	0.001320	0.001183	0.001065
30	0.000962	0.000872	0.000793	0.000723	0.000661	0.000606	0.000557	0.000513	0.000473	0.000438
40	0.000406	0.000377	0.000351	0.000327	0.000305	0.000285	0.000267	0.000250	0.000235	0.000221

At values of the temperature less than $\Theta_D/100$, the Debye theory can be relied upon to give correctly the contribution to the heat capacity attributable to lattice vibrations. In some cases it holds well at temperatures up to $\Theta_D/50$. At these low temperatures the Debye expression for C_V reduces to

$$C_V = \frac{12\pi^4 R}{5\Theta_D^3} \cdot T^3 \quad (4e-7)$$

or

$$C_V = 124.8 \frac{mJ}{\text{mole} \cdot \text{K}} \left(\frac{T}{\Theta_D} \right)^3 \quad (4e-8)$$

For metals there is a contribution to the heat capacity due to the free electrons equal to γT , where γ is known as the electronic constant. The total heat capacity of a metal is therefore

$$C_V = \frac{12\pi^4 R}{5\Theta_D^3} \cdot T^3 + \gamma T \quad (4e-9)$$

The most reliable values of Θ_D and γ are obtained from heat-capacity measurements in the liquid helium region. It is customary in such work to plot C_V/T against T^2 . On such a plot a nonmetal gives a straight line through the origin, whereas a metal gives a straight line with a positive intercept.

Values of Θ_D and γ are given in Table 4e-10. They were obtained in almost all cases by calorimetric measurements in the liquid helium range or lower. Values of Θ_D are given in kelvins, and those of γ in millijoules per mole kelvin squared.

TABLE 4e-10. VALUES OF Θ_D AND γ , IN THE HEAT-CAPACITY EQUATION (4e-9).

Substance	Symbol	Θ_D , K	γ , $\frac{mJ}{\text{mole} \cdot \text{K}^2}$	Refs.
Aluminum.....	Al	428	1.35	1, 2, 89
Antimony.....	Sb	211	0.112	3
Argon.....	A	93		
Arsenic.....	As	282	0.19	3, 4
Barium.....	Ba	110	2.7	5
Beryllium.....	Be	1440	0.17	6, 7
Bismuth.....	Bi	119	0.021	8, 9
Bismuth telluride.....	Bi ₂ Te ₃	155	31
Cadmium.....	Cd	209	0.69	10
Calcium.....	Ca	230	2.9	11, 5
Calcium fluoride.....	CaF ₂	510	32
Carbon (graphite).....	C	420	12
Carbon (diamond).....	C	2230	13, 14, 90
Cesium.....	Cs	38	3.2	15
Chlorine.....	Cl	115		
Chromium.....	Cr	630	1.40	16
Cobalt.....	Co	445	4.7	17, 18, 19
Copper.....	Cu	343	0.688	20, 21, 22, 54
Dysprosium.....	Dy	210	23
Gadolinium.....	Gd	195	93
Gallium.....	Ga	320	0.60	10, 24
Germanium.....	Ge	370	25, 26
Germanium telluride.....	GeTe	166	1.32	85
Gold.....	Au	165	0.69	20, 27, 91
Hafnium.....	Hf	252	2.16	28
Helium ⁴ (hep).....	He ⁴ (hep)	26.4	84
Helium ³ (bcc).....	He ³ (bcc)	16		
Hydrogen.....	H	105		
Hydrogen ²	H ²	97		
Ice.....	H ₂ O	192		
Indium.....	In	108	1.6	29, 30
Indium antimonide.....	InSb	200	44
Iodine.....	I	106		
Iridium.....	Ir	420	3.1	59
Iron.....	Fe	467	5.0	60, 61, 92
Iron oxide.....	Fe ₂ O ₃	660	33
Iron selenide.....	FeSe ₂	366	66
Iron sulfide.....	FeS ₂	637	66
Krypton.....	Kr	72		
Lanthanum.....	La	142	10	62, 95
Lead.....	Pb	105	3.0	56
Lead selenide.....	PbSe	135-160		
Lead sulfide.....	PbS	194		
Lead telluride.....	PbTe	124-135		
Lithium.....	Li	344	1.63	15
Lithium chloride.....	LiCl	422	86
Lithium fluoride.....	LiF	732	34, 35, 36
Magnesium.....	Mg	400	1.3	63, 64
Magnesium cadmide.....	Mg ₃ Cd	290	0.8	37
Magnesium oxide.....	MgO	946	38
Manganese.....	Mn	410	14	48, 49, 50
Mercury.....	Hg	71.9	1.79	65, 75
Molybdenum.....	Mo	450	2.0	59, 67, 68, 94
Neon.....	Ne	75	45
Nickel.....	Ni	450	7.1	16, 69
Nickel selenide.....	NiSe ₂	297	66
Niobium.....	Nb	275	7.79	52, 58, 94

TABLE 4e-10. VALUES OF Θ AND γ , IN THE HEAT-CAPACITY EQUATION (4e-9)
(Continued)

Substance	Symbol	Θ_D , K	γ , $\frac{mJ}{\text{mole} \cdot \text{K}^2}$	Refs.
Niobium-tin.....	Nb ₃ Sn	228	13.1	87
Nitrogen.....	N	68		
Osmium.....	Os	500	2.4	59
Oxygen.....	O	91		
Palladium.....	Pd	274	9.42	53
Platinum.....	Pt	240	6.8	27
Potassium.....	K	91	2.1	15
Potassium bromide.....	KBr	174	39
Potassium chloride.....	KCl	235	39, 40, 41
Potassium fluoride.....	KF	330	86
Potassium iodide.....	KI	132	39
Rhenium.....	Re	430	2.3	59, 70, 94
Rhodium.....	Rh	480	4.9	59
Rubidium.....	Rb	56	2.4	15
Rubidium bromide.....	RbBr	131	86
Rubidium chloride.....	RbCl	165	86
Rubidium iodide.....	RbI	103	86
Ruthenium.....	Ru	600	3.3	59
Scandium.....	Sc	360	10.7	46, 96
Selenium.....	Se	90	71
Silicon.....	Si	640	25, 26
Silicon dioxide.....	SiO ₂	470	42
Silver.....	Ag	225	0.650	54
Silver bromide.....	AgBr	144		
Silver chloride.....	AgCl	183		
Sodium.....	Na	158	1.4	5, 72, 73
Sodium bromide.....	NaBr	225	86
Sodium chloride.....	NaCl	321	39
Sodium fluoride.....	NaF	492	86
Sodium iodide.....	NaI	164	39
Strontium.....	Sr	147	3.6	5
Tantalum.....	Ta	240	5.9	59, 68, 74, 94
Tellurium.....	Te	153	71
Thallium.....	Tl	78.5	1.47	75
Thorium.....	Th	163	4.3	76, 97
Tin (white).....	Sn	199	1.78	67, 77, 78
Tin (gray).....	Sn	210	41
Titanium.....	Ti	420	3.5	28, 79, 80
Titanium dioxide.....	TiO ₂	760	43
Tungsten.....	W	400	1.3	59, 68, 81
Uranium.....	U	207	10.0	57, 97
Uranium dioxide.....	UO ₂	160		
Vanadium.....	V	380	9.8	47
Xenon.....	Xe	64	45
Yttrium.....	Y	280	10.2	51, 94
Yttrium iron garnet.....	YIG	510		
Zinc.....	Zn	327	0.65	24, 82, 83
Zinc sulfide.....	ZnS	315	35
Zirconium.....	Zr	291	2.80	28

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