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# THIRTY-SECOND ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED DURING 1925

By Gregory Paul Baxter

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The fifth Report of the German Committee on Atomic Weights[1] has been published, and the second report of the International Committee on Chemical Elements[2] covering atomic weights. The latter has been criticized by Moles.[3]

**Helium.**—Baxter and Starkweather[4] have redetermined the density

The Density of Helium
0° and 760 mm.

| Series | No. of treatments with adsorbent | Globe 1 1031.51 Ml. | Globe 2 1029.30 Ml. | Globe 3 1038.48 Ml. | Av. |
|---|---|---|---|---|---|
| 1 | 3 | (0.17853) | (0.17850) | (0.17858) | (0.17854) |
| 2 | 5 | .17840 | .17848 | .17844 | .17844 |
| 3 | 6 | .17844 | .17845 | .17848 | .17846 |
| 4 | 7 | .17848 | .17841 | .17848 | .17846 |
|  | Av. | .17844 | .17845 | .17847 | .17845 |
|  |  | Globe 4 2111.0 Ml. | Globe 5 2117.6 Ml. |  |  |
| 7 | 9 | 0.17853 | 0.17841 |  | .17847 |
| 8 | 10 | .17849 | .17851 |  | .17850 |
| 9 | 11 | .17846 | .17852 |  | .17849 |
| 10 | 11 | .17842 | .17843 |  | .17843 |
| 11 | 14 | .17846 | .17846 |  | .17846 |
| 12 | 14 | .17846 | .17845 |  | .17846 |
|  | Av. | .17847 | .17846 |  | .17847 |

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[1] *Ber.*, **58B**, I (1925).

[2] This Journal, **47**, 597 (1925).

[3] Moles, *Anal. soc. españ. fís. quim.*, **23**, 164 (1925).

[4] Baxter and Starkweather, *Proc. Nat. Acad. Sci.*, 11, 231 (1925); **12,** 20 (1926); *Carnegie Inst. Yearbook*, **24**, 299 (1925).

of helium at one and at one-half atmosphere.[3] Chemical purification was followed by fractional adsorption on dehydrated chabazite at the temperature of liquid air. The results are referred to sea level, Lat. 45°.

In Series 1 the gas was found to be slightly impure. The average of Series 2–12 is 0.17846.

0° and 380 mm.

| Series | No. of treatments with adsorbent | Globe 4 | Globe 5 | Av. |
|---|---|---|---|---|
| 13 | 14 | (0.08931) | 0.08922 | 0.08922 |
| 14 | 14 | .08924 | .08924 | .08924 |
| 15 | 16 | .08923 | .08923 | .08923 |
| 16 | 18 | .08925 | .08922 | .08924 |
| | | .08924 | 0.8923 | .08923 |

The results at one half atmosphere indicate that no correction for deviation from Boyle's law is necessary. With the density of oxygen 1.42898 found by Baxter and Starkweather[5] the atomic weight of helium for different values of the coefficient of deviation from Boyle's law for oxygen becomes

| $\frac{(PV)_0}{(PV)_1}$ (oxygen) | Limiting value of molal volume | At. wt. He |
|---|---|---|
| 1.00090 | 22.4137 | 3.9999 |
| 1.00100 | 22.4160 | 4.0004 |

**Boron.**—Briscoe, Robinson and Stephenson,[6] have shown that borax loses alkali during fusion and, therefore, that fused borax is unsuited for use in the determination of the atomic weight of boron.

Briscoe and Robinson[7] synthesized boron trichloride from boron and chlorine. The boron was prepared from boric oxide and magnesium and was extracted with hydrochloric acid. Treatment of the boron trichloride with mercury and sodium amalgam was combined with careful fractionation in dry air and finally in exhausted glass apparatus, while the final products were collected in sealed glass bulbs. After solution in water comparison with silver in the usual way followed. Weights are in vacuum; Cl = 35.457.

Atomic Weight of Boron

| Wt. of $BCl_3$ | Wt. of Ag | Ratio $BCl_3 : 3Ag$ | At. wt. B |
|---|---|---|---|
| 7.10616 | 19.61748 | 0.362236 | 10.854 |
| 8.06893 | 22.28012 | .362158 | 10.829 |
| 9.91393 | 27.37313 | .362177 | 10.835 |
| 7.42801 | 20.49990 | .362344 | 10.889 |
| | Av. | .362229 | 10.852 |

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[5] Corrected for small error in the assumption of *g* at Cambridge.

[6] Briscoe, Robinson and Stephenson, *J. Chem. Soc.*, **127**, 150 (1925).

[7] Briscoe and Robinson, *J. Chem. Soc.*, **127**, 696 (1925).

### Boron from Tuscany

| Wt. of $BCl_3$ | Wt. of Ag | Ratio $BCl_3 : 3Ag$ | At. wt. B |
|---|---|---|---|
| 7.73567 | 21.35379 | 0.362262 | 10.862 |
| 9.83151 | 27.14230 | .362221 | 10.849 |
| 7.88427 | 21.76764 | .362201 | 10.843 |
| 6.61346 | 18.26253 | .362133 | 10.821 |
| 7.51389 | 20.74865 | .362139 | 10.823 |
| | | Av. .362191 | 10.840 |

### Boron from Asia Minor

| | | | |
|---|---|---|---|
| 7.88217 | 21.76472 | 0.362153 | 10.827 |
| 7.00794 | 19.35154 | .362139 | 10.823 |
| 11.56846 | 31.94600 | .362126 | 10.818 |
| 5.96256 | 16.46538 | .362127 | 10.819 |
| 5.83978 | 16.12666 | .362120 | 10.816 |
| 5.31851 | 14.68670 | .362131 | 10.820 |
| 12.04670 | 33.26752 | .362116 | 10.815 |
| 11.39071 | 31.45640 | .362111 | 10.814 |
| 8.45278 | 23.34215 | .362125 | 10.818 |
| | | Av. .362128 | 10.819 |

### Boron from California

| | | | |
|---|---|---|---|
| 9.93543 | 27.42992 | 0.362212 | 10.846 |
| 6.69247 | 18.47861 | .362174 | 10.834 |
| 6.87297 | 18.97723 | .362169 | 10.832 |
| 2.94096 | 8.11982 | .362195 | 10.841 |
| 4.86840 | 13.44182 | .362184 | 10.837 |
| 4.89699 | 13.52005 | .362202 | 10.843 |
| 5.72597 | 15.80980 | .362179 | 10.836 |
| 9.24458 | 25.52406 | .362190 | 10.839 |
| 4.69097 | 12.95092 | .362211 | 10.846 |
| 8.66792 | 23.92939 | .362229 | 10.852 |
| 8.08918 | 22.32812 | .362287 | 10.870 |
| 5.95008 | 16.42010 | .362366 | 10.896 |
| | | Av. .362217 | 10.848 |

The authors see evidence in these results (1) of isotopic separation during distillation, (2) of a difference in atomic weight among samples of boron from different geographical sources.

**Carbon.**—Dean[8] reduced precipitated silver cyanide, dried in a vacuum and then in air at 100°, by heating in hydrogen. Weights are in vacuum; N = 14.008.

### Atomic Weight of Carbon
### Series A (Glass Vessels)

| Wt. of AgCN | Wt. of Ag | Ratio Ag: AgCN | At. wt. C |
|---|---|---|---|
| 8.09287 | 6.52019 | 0.805671 | 12.013 |
| 11.27484 | 9.08419 | .805704 | 12.007 |
| 16.31000 | 13.41112 | .805709 | 12.006 |
| 13.58968 | 10.94942 | .805715 | 12.005 |

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[8] Dean, *J. Chem. Soc.*, **125**, 2656 (1924).

Atomic Weight of Carbon (*Continued*)

| Wt. of AgCN | Wt. of Ag | Ratio Ag: AgCN | At. wt. C |
|---|---|---|---|
| 13.63559 | 10.98669 | .805736 | 12.002 |
| 13.00330 | 10.47853 | .805836 | 11.985 |
| 11.25209 | 9.06669 | .805778 | 11.995 |
| 19.59057 | 15.78523 | .805757 | 11.999 |
| 10.74440 | 8.65677 | .805701 | 12.008 |
| 10.48999 | 8.45191 | .805712 | 12.006 |
| | Av. | .805732 | 12.003 |

Series B (Silica Vessels)

| | | | |
|---|---|---|---|
| 12.78888 | 10.30454 | 0.805742 | 12.000 |
| 12.34522 | 9.94716 | .805750 | 12.000 |
| 13.55745 | 10.92354 | .805722 | 12.004 |
| 11.57833 | 9.32901 | .805730 | 12.003 |
| 13.22384 | 10.65417 | .805679 | 12.012 |
| 11.02014 | 8.87968 | .805768 | 11.997 |
| | Av. | .805732 | 12.003 |

Series B (Fractionated AgCN)

| Fraction | Wt. of AgCN | Wt. of Ag | Ratio Ag: AgCN | At. wt. C |
|---|---|---|---|---|
| F | 10.65300 | 8.58302 | 0.805690 | 12.010 |
| F | 12.87330 | 10.37157 | .805665 | 12.014 |
| E | 7.18106 | 5.78649 | .805798 | 11.992 |
| G | 8.45664 | 6.81430 | .805792 | 11.993 |
| G | 10.82781 | 8.72440 | .805740 | 12.001 |
| | | Av. | .805737 | 12.002 |

Silver cyanate was precipitated by means of sulfuric acid from solution in ammonia, dried in a vacuum and reduced in hydrogen, eventually at 310°

Series A

| Wt. of AgCNO | Wt. of Ag | Ratio Ag: AgCNO | At. wt. C |
|---|---|---|---|
| 9.06436 | 6.52393 | 0.719734 | 12.001 |
| 6.32084 | 4.54946 | .719756 | 11.996 |
| 8.62108 | 6.20492 | .719738 | 12.000 |
| 6.86108 | 4.93828 | .719753 | 11.997 |
| 14.74115 | 10.61003 | .719756 | 11.996 |
| 10.58756 | 7.61992 | .719705 | 12.007 |
| 9.85865 | 7.09569 | .719742 | 11.999 |
| 10.80524 | 7.77683 | .719728 | 12.002 |
| | Av. | .719739 | 12.000 |

Series B

| | | | |
|---|---|---|---|
| 10.95568 | 7.88354 | 0.719585 | 12.032 |
| 15.41320 | 11.09163 | .719619 | 12.025 |
| 15.88829 | 11.43487 | .719704 | 12.007 |
| 7.36851 | 5.30337 | .719734 | 12.001 |
| 7.44756 | 5.36002 | .719701 | 12.008 |
| 12.52765 | 9.01405 | .719532 | 12.043 |
| 13.47481 | 9.69587 | .719555 | 12.038 |
| 18.29697 | 13.16456 | .719494 | 12.051 |
| 18.22897 | 13.11874 | .719664 | 12.015 |
| | Av. | .719621 | 12.024 |

SERIES C

| Wt. of AgCNO | Wt. of Ag | Ratio Ag: AgCNO | At. wt. C |
|---|---|---|---|
| 11.75141 | 8.45731 | 0.719685 | 12.011 |
| 11.93035 | 8.58648 | .719717 | 12.004 |
| 10.73580 | 7.72683 | .719726 | 12.003 |
| 5.01536 | 3.60973 | .719734 | 12.000 |
| | | Av. .719716 | 12.005 |

From these results Dean finds Ag = 107.871 and CN = 26.008.

**Oxygen.**—Batuecas, Maverick and Schlatter[9] with a slightly modified apparatus have continued the work of Batuecas on deviations of gases from Boyle's law for the range 0–1 atmosphere. For oxygen $(PV)_0/(PV)_1$ is found to be

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Series I | 1.00093 | (1.00051) | 1.00096 | 1.00089 | | | |
| Series II | (1.00056) | 1.00094 | 1.00068 | 1.00093 | (1.00052) | 1.00074 | Av. 1.00087 |

**Aluminum.**—Krepelka and Nikolic[10] prepared anhydrous aluminum chloride by ignition of the oxide with carbon in a current of chlorine, and after fractional distillation in exhausted glass apparatus collected the product in sealed glass bulbs. The contents of the bulbs were compared with silver and in two experiments the silver chloride was collected and weighed.

Weights are in vacuum; Cl = 35.457.

THE ATOMIC WEIGHT OF ALUMINUM

| Wt. of $AlCl_3$ | Wt. of Ag | Ratio $AlCl_3 : 3Ag$ | At. wt. Al | Wt. of AgCl | Ratio $AgCl_3 : 3AgCl$ | At. wt. Al |
|---|---|---|---|---|---|---|
| 1.35387 | 3.28594 | 0.412019 | 26.975 | | | |
| 0.97967 | 2.37778 | .412010 | 26.972 | 3.15924 | 0.310087 | 26.974 |
| 1.10277 | 2.67642 | .412032 | 26.979 | 3.55632 | .310088 | 26.970 |
| 0.92155 | 2.23672 | .412009 | 26.972 | | | |
| 1.97000 | 4.78148 | .412006 | 26.971 | | | |
| | Av. | .412015 | 26.974 | | .310092 | 26.972 |

The result is essentially identical with that of Krepelka's earlier analysis of aluminum chloride.

**Silicon.**—Jaeger and Dykstra[11] have compared the density of tetraethylsilicane prepared from terrestrial and meteoric material and found no differences greater than the experimental error.

**Chlorine.**—Batuecas[12] prepared methyl chloride (1) by action of phosphorus trichloride on methyl alcohol and (2) by thermal decomposition of tetramethylammonium chloride, both followed by fractionation. Density determinations at 0° gave the following results.

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[9] Batuecas, Maverick and Schlatter, *J. chim. phys.*, **22**, 131 (1925).

[10] Krepelka and Nikolic, *Chem. Listy*, **19**, 158 (1925).

[11] Jaeger and Dykstra, *Z. anorg. allgem. Chem.*, **143**, 252 (1925).

[12] Batuecas, *Compt. rend.*, **180**, 1929 (1925); *Anal. soc. españ. fís. quim.*, **23**, 343 (1925).

WEIGHT OF NORMAL LITER

| Method of preparation | Globe N3 772.39 | Globe III 220.26 | Av. |
|---|---|---|---|
| 1 | 2.3099 | 2.3082 | 2.3090 |
| 1 | 2.3092 | 2.3095 | 2.3094 |
| 1 | 2.3081 | 2.3096 | 2.3088 |
| 1 | 2.3087 | 2.3094 | 2.3090 |
| 1 | 2.3096 | 2.3098 | 2.3097 |
| 2 | 2.3077 | 2.3080 | 2.3079 |
| 2 | 2.3073 | 2.3073 | 2.3073 |
| 2 | 2.3077 | 2.3080 | 2.3078 |
| 2 | 2.3072 | 2.3080 | 2.3072 |

The general average, 2.3048, is notably higher than that found by Baumé, 2.3045.

Batuecas[13] also measured the compressibility of methyl chloride at 0° and low pressures and finds $(PV)_0/(PV)_1 = 1.0247$. If the density of the vapor is taken as 2.3084, Cl = 35.470.

**Chlorine.**—Harkins and Jenkins[14] by diffusion of hydrochloric acid have obtained chlorine of atomic weight 35.418. Weights are in vacuum.

ORDINARY CHLORINE

| Wt. of Ag | Wt. of AgCl | Ratio AgCl : Ag | At. wt. Cl |
|---|---|---|---|
| 1.78992 | 2.37824 | 1.32868 | 35.458 |
| 2.09738 | 2.78678 | 1.32869 | 35.459 |
| 1.66813 | 2.21636 | 1.32865 | 35.455 |
| 1.86118 | 2.47288 | 1.32866 | 35.456 |
| | Av. | 1.32867 | 35.457 |

DIFFUSED CHLORINE

| Wt. of Ag | Wt. of AgCl | Ratio AgCl : Ag | At. wt. Cl |
|---|---|---|---|
| 1.32078 | 1.75437 | 1.32838 | 35.415 |
| 1.16019 | 1.54108 | 1.32830 | 35.417 |
| 1.42781 | 1.89659 | 1.32832 | 35.419 |
| 1.43282 | 1.90321 | 1.32830 | 35.417 |
| 1.05716 | 1.40424 | 1.32832 | 35.419 |
| 1.75764 | 2.33470 | 1.32832 | 35.419 |
| | Av. | 1.32831 | 35.418 |

Harkins and Stone[15] have compared chlorine from wernerite and chlorine from lawrencite (meteoric) with ordinary chlorine by synthesis of silver chloride.

Menzies[16] has found the chlorine in "shale balls" associated with the Canyon Diablo meteorite to be identical with ordinary chlorine within the limit of error of the experiment (1/2000).

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[13] Batuecas, *Compt. rend.*, **181**, 40 (1925).

[14] Harkins and Jenkins, *Proc. Nat. Acad. Sci.*, **11**, 624 (1925); THIS JOURNAL, **48**, 58 (1926).

[15] Harkins and Stone, *Proc. Nat. Acad. Sci.*, **11**, 643 (1925); *Nature*, **116**, 426 (1925).

[16] Menzies, *Nature*, **116**, 643 (1925).

ATOMIC WEIGHT OF CHLORINE

AgCl : Ag

| | Ordinary | | Wernerite | Lawrencite |
|---|---|---|---|---|
| | 1.32868 | Harkins and Jenkins | 1.32866 | 1.32866 |
| | 1.32869 | | 1.32867 | 1.32868 |
| | 1.32865 | | | 1.32869 |
| | 1.32866 | | | 1.32869 |
| | 1.32869 | | | 1.32865 |
| | 1.32868 | | | |
| Av. | 1.32868 | | 1.32867 | 1.32867 |
| At. wt. Cl | 35.457 | | 35.457 | 35.457 |

**Copper.**—Ruer and Bode[17] defend their work on copper oxide against criticisms by the German Committee on Atomic Weights.

**Germanium.**—Baxter and Cooper[18] synthesized germanium tetrabromide from pure germanium and bromine. The bromide was subjected to elaborate fractional distillation in vacuum and was collected in sealed glass bulbs. The contents of the bulbs were compared with silver in the usual way and the silver bromide was collected and weighed. Weights are in vacuum; Br = 79.916. The fractions are numbered in the order of decreasing volatility.

ATOMIC WEIGHT OF GERMANIUM

| Fraction | Wt. of $GeBr_4$ | Wt. of Ag | Ratio $GeBr_4 : 4Ag$ | At. wt. of Ge | Wt. of AgBr | Ratio $GeBr_4 : 4AgBr$ | At. wt. of Ge |
|---|---|---|---|---|---|---|---|
| 6 | 6.39771 | 7.03812 | 0.909008 | 72.591 | 12.25222 | 0.522167 | 72.579 |
| 25 | 6.79020 | 7.47014 | .908979 | 72.579 | 13.00431 | .522150 | 72.567 |
| 7 | 10.89713 | 11.98757 | .909036 | 72.603 | 20.86782 | .522198 | 72.603 |
| 24 | 7.72394 | 8.49797 | (.908916) | (72.551) | 14.79244 | (.522155) | (72.570) |
| 8 | 9.90366 | 10.89584 | (.908940) | (72.562) | 18.96671 | (.522160) | (72.574) |
| 23 | 11.17556 | 12.29411 | .909017 | 72.595 | 21.40092 | .522200 | 72.604 |
| 10 | 9.59408 | 10.55426 | .909024 | 72.598 | 18.37224 | .522205 | 72.608 |
| 21 | 10.69340 | 11.76356 | .909028 | 72.600 | 20.47681 | .522220 | 72.619 |
| 11 | 10.71709 | 11.79004 | .908995 | 72.586 | 20.52351 | .522186 | 72.594 |
| 20 | 11.79501 | 12.97604 | .908984 | 72.581 | 22.58717 | .522200 | 72.604 |
| 12 | 10.50295 | 11.55444 | .908997 | 72.586 | 20.11291 | .522199 | 72.604 |
| 19 | 11.94787 | 13.14369 | .909019 | 72.596 | 22.88031 | .522190 | 72.597 |
| 13 | 10.11814 | 11.13066 | .909033 | 72.602 | 19.37580 | .522205 | 72.608 |
| 18 | 8.38344 | 9.22244 | .909026 | 72.599 | 16.05400 | .522203 | 72.607 |
| 14 | 9.93784 | 10.93219 | .909044 | 72.607 | 19.03050 | .522206 | 72.609 |
| 16 | 9.28357 | 10.21256 | .909035 | 72.603 | 17.77797 | .522195 | 72.601 |
| | | Av. | .909016 | 72.595 | | .522195 | 72.601 |

The final average, 72.598, is essentially identical with that found by Baxter and Cooper by analysis of the tetrachloride.

**Selenium.**—Bruylants, Lafortune and Verbruggen[19] have determined the density of hydrogen selenide with very great care. The gas employed in the reliable determinations was prepared either by decomposition of aluminum selenide with water or by synthesis from the elements, followed

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[17] Ruer and Bode, *Ber.*, **58B**, 852 (1925).

[18] Baxter and Cooper. *Proc. Am. Acad. Arts Sci.*, **60**, 219 (1925); *J. Phys. Chem.*, **29**, 1364 (1925).

[19] Bruylants, Lafortune and Verbruggen, *Bull. soc. chim. Belg.*, **33**, 587 (1924).

by fractional distillation. Pure and crude selenium yielded nearly identical results. In the following tables the values are not corrected to standard gravity, but are corrected for deviations from Boyle's law to 760, 506.67 and 253.33 mm., respectively.

DENSITY OF SELENIUM HYDRIDE

Pressure 760 mm.

| Series | Globe 1 762.949 Ml. | Globe 2 498.401 Ml. | Globe 3 400.348 Ml. | Globe 4 407.968 Ml. | Globe 5 412.175 Ml. | Globe 6 295.019 Ml. | Globe 7 204.082 Ml. |
|---|---|---|---|---|---|---|---|
| 1 | 3.66380 | 3.66366 | 3.66458 | | | | |
| 2 | 3.66449 | | | 3.66323 | 3.66396 | | |
| 3 | 3.66351 | | | 3.66378 | 3.66376 | 3.66325 | 3.66400 |
| 4 | 3.66472 | | | 3.66416 | 3.66452 | 3.66356 | 3.66486 |
| 5 | 3.66546 | | | 3.66607 | 3.66676 | 3.66586 | 3.66504 |
| 6 | 3.66433 | 3.66374 | 3.66417 | | | | |
| 7 | 3.66412 | 3.66430 | 3.66451 | | | | |
| 8 | 3.66408 | 3.66433 | 3.66354 | | | | |
| 9 | 3.66466 | | | 3.66412 | 3.66484 | | |
| 10 | 3.66427 | 3.66379 | 3.66518 | | | | |
| 11 | 3.66509 | 3.66519 | | | | | |
| 12 | 3.66112 | | | 3.66052 | 3.65661 | | |
| 13 | 3.65951 | | | | | | |
| 14 | 3.66298 | | | 3.66377 | 3.66479 | | |
| 15 | 3.66403 | | | 3.66543 | 3.66543 | | |
| 16 | 3.66438 | 3.66461 | 3.66512 | | | | |
| 17 | 3.66392 | 3.66356 | | | | | |
| 18 | 3.66337 | | | | | | |
| 19 | 3.66442 | | | 3.66473 | 3.66514 | 3.66464 | 3.66442 |
| 20 | 3.66435 | | | 3.66455 | 3.66448 | 3.66439 | 3.66474 |
| 21 | 3.66497 | | | 3.66453 | 3.66577 | | |
| 22 | 3.66411 | 3.66476 | | | | | |
| 23 | 3.65170 | | | 3.65765 | 3.65648 | 3.65515 | 3.65647 |
| 24 | 3.65541 | | | 3.65795 | 3.65773 | 3.65830 | 3.66015 |
| 25 | 3.65689 | | | 3.65982 | 3.66061 | 3.65980 | 3.66159 |
| 26 | 3.66016 | | | 3.66061 | 3.66132 | | |
| 27 | 3.66279 | | | 3.66326 | 3.66409 | 3.66268 | 3.66396 |
| 28 | 3.65337 | | | 3.65375 | 3.66496 | 3.66262 | 3.66485 |
| 29 | 3.66204 | | | 3.66203 | 3.66216 | 3.66072 | 3.66221 |
| 30 | 3.65376 | | | 3.65322 | | 3.65363 | 3.65379 |
| 31 | 3.66339 | | | 3.65878 | | 3.65834 | 3.66136 |

Pressure = 506.67 mm.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 32 | 3.64891 | | | 3.64913 | 3.64840 | 3.64857 | 3.64847 |
| 33 | 3.64818 | | | 3.64859 | 3.64793 | 3.64829 | 3.64776 |
| 34 | 3.64690 | 3.64527 | 3.64614 | | | | |
| 35 | 3.65439 | | | 3.65382 | 3.65542 | | |
| 36 | 3.64848 | 3.64928 | 3.64841 | | | | |
| 37 | 3.64891 | | | 3.65053 | | | |
| 38 | 3.64775 | 3.64732 | 3.64834 | | | | |
| 39 | 3.64989 | 3.64955 | 3.64904 | | | | |

DENSITY OF SELENIUM HYDRIDE (*Concluded*)

Pressure = 253.33 mm.

| Series | Globe 1 762.949 Ml. | Globe 2 498.401 Ml. | Globe 3 400.348 Ml. | Globe 4 407.968 Ml. | Globe 5 412.175 Ml. | Globe 6 295.019 Ml. | Globe 7 204.082 Ml. |
|---|---|---|---|---|---|---|---|
| 40 | 3.63470 | | | 3.63387 | 3.63633 | 3.63543 | 3.63771 |
| 41 | 3.63448 | | | 3.63488 | 3.63446 | 3.63404 | |
| 42 | 3.63448 | | | 3.63521 | 3.63563 | 3.63461 | 3.63734 |
| 43 | 3.63597 | | | 3.64099 | 3.64021 | 3.63916 | |
| 44 | 3.63450 | | | 3.63334 | | 3.63286 | 3.63667 |
| 45 | 3.63570 | | | 3.63541 | 3.63478 | 3.63421 | 3.63493 |
| 46 | 3.64189 | 3.64319 | | | | | |
| 47 | 3.63514 | 3.63532 | 3.63625 | | | | |
| 48 | 3.63689 | | | 3.63783 | 3.63723 | | |
| 49 | 3.63245 | 3.63651 | | | | | |
| 50 | 3.63510 | 3.63238 | 3.63708 | | | | |

Series 5, 35, 46 and 48 are rejected because of probable error in pressure determination. Series 12, 13, 14, 15, 23, 24, 25, 26, 27, 28, 29, 30, 31 and 37 are rejected because of known impurity in the gas. After these rejections the averages become

| Mm. | 760 | 506.67 | 253.33 |
|---|---|---|---|
| Av. | 3.66431 | 3.64820 | 3.63549 |

whence $(PV)_0/(PV)_1 = 1.01053$.

Assuming $g$ at Louvain to be 981.128 and the density and deviation from Boyle's law for oxygen to be 1.4289 and 1.00097, respectively, $H_2Se = 81.243$ and $Se = 79.23$.

**Bromine.**—Robinson and Briscoe[20] in an attempt to separate the isotopes of bromine subjected ammonium bromide to 80 series of crystallizations involving 2700 crystallizations in all. The extreme end fractions were then rejected and the penultimate fractions at head and tail were subjected to analysis. After careful elimination of chloride and iodide, silver bromide was quantitatively synthesized from weighed amounts of silver. No difference could be detected between the two samples of bromide. Weights are in vacuum.

ATOMIC WEIGHT OF BROMINE

| More Soluble Fraction | | | | Less Soluble Fraction | | | |
|---|---|---|---|---|---|---|---|
| Wt. of Ag | Wt. of AgBr | Ratio Ag: AgBr | At. wt. Br | Wt. of Ag | Wt. of AgBr | Ratio Ag : AgBr | At. wt. Br |
| 3.69267 | 6.42874 | 0.574400 | 79.933 | 5.14584 | 8.95708 | 0.574499 | 79.901 |
| 5.05818 | 8.80494 | .574471 | 79.910 | 3.08029 | 5.36261 | .574401 | 79.933 |
| 3.93141 | 6.84337 | .574484 | 79.906 | 3.34559 | 5.82369 | .574479 | 79.907 |
| 3.67235 | 6.39249 | .574479 | 79.908 | 3.43566 | 5.98102 | .574427 | 79.916 |
| | Av. | .574459 | 79.914 | | | .574451 | 79.914 |

**Antimony.**—Schreiner[21] in eight comparisons of antimony tribromide with silver finds Sb = 121.73.

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[20] Robinson and Briscoe, *J. Chem. Soc.*, **127**, 138 (1925).

[21] Schreiner, *Tids. Kemi Bergvaesen*, **4**, 63, 89 (1925).

**Holmium.**—Driggs and Hopkins[22] fractionated holmium-rich material as bromate and as basic nitrate until determinations of magnetic susceptibility showed the material to be free from yttrium and dysprosium. The purified oxide was converted into anhydrous chloride and after the chloride had been weighed it was dissolved and compared with silver. Weights are in vacuum; Cl = 35.457.

ATOMIC WEIGHT OF HOLMIUM

| Wt. of $HoCl_3$ | Wt. of Ag | | Ratio $HoCl_3 : 3Ag$ | At. wt. of Ho |
|---|---|---|---|---|
| 0.87393 | 1.04789 | | 0.83399 | 163.54 |
| .28290 | 0.33929 | | .83379 | 163.48 |
| .43914 | .52663 | | .83386 | 163.50 |
| .73784 | .88498 | | .83373 | 163.46 |
| .42703 | .51224 | | .83365 | 163.43 |
| .26736 | .32071 | | .83365 | 163.43 |
| | | Av. | *.83378* | *163.47* |

This result confirms Holmberg's original value 163.5.

**Hafnium.**—Hönigschmid and Zintl[23] prepared hafnium bromide, from material which had been subjected to more than 5000 crystallizations of hafnium potassium fluoride, by heating the oxide with carbon in a current of nitrogen charged with bromide. After several sublimations in a vacuum the material was collected in sealed glass bulbs. These were weighed, broken under water and after the glass had been weighed, the solution of hafnium bromide was precipitated with an excess of silver and finally the silver bromide was collected and weighed. Weights are in vacuum; Br = 79.916; Zr = 91.22.

| Sample of $HfBr_4$ | Wt. of $HfBr_4$ | Wt. of AgBr | | Ratio $HfBr_4 : 4AgBr$ | At. wt. of Hf |
|---|---|---|---|---|---|
| III | 1.50702 | 2.27562 | | 0.66225 | 177.80 |
| | 1.32549 | 2.00162 | | .66221 | 177.78 |
| | | | Av. | .66223 | 177.79 |
| I and II | 1.33538 | 2.01436 | | .66293 | 178.32 |
| | 1.07786 | 1.62580 | | .66297 | 178.35 |
| | | | Av. | .66295 | 178.33 |

The above values are corrected for known zirconium content.

| Sample | $ZrO_2$ in $HfO_2$, % | Corr. at. wt. of Hf |
|---|---|---|
| III | 0.57 | 178.64 |
| II and I | .16 | 178.57 |

This result is lower than the value previously obtained by Hönigschmid and Zintl from considerably less pure material.

**Gold.**—Hönigschmid and Zintl[24] compared solutions of weighed

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[22] Driggs and Hopkins. THIS JOURNAL, **47**, 363 (1925).

[23] Hönigschmid and Zintl. *Ber.*, **58B**, 453 (1925).

[24] Hönigschmid and Zintl. *Z. anorg. allgem. Chem.*, **147**, 262 (1925).

amounts of the chloride of common and "artificial" gold (Miethe and Stammreich) by electrometric titration with a solution of titanium trichloride. Within the limit of error of the experiment no difference between the two materials could be detected.

**Lead.**—Gleditsch, Dorenfeldt and Berg[25] have compared the atomic weights of common and uranium lead from cleveite (Aust-Agder, Norway) by converting lead chloride quantitatively into lead sulfate and by determining the densities of saturated solutions of the nitrates; Cl = 35.46; S = 32.06.

Atomic Weight of Lead

| Sample | Wt. of $PbCl_2$ | Wt. of $PbSO_4$ | Ratio | At. wt. of Pb |
|---|---|---|---|---|
| Common | 0.7580 | 0.8265 | | 207.27 |
| | .7727 | .84255 | | 207.18 |
| | | | Av. | 207.22 |
| Cleveite | .97615 | 1.06470 | | 206.22 |
| | 1.71490 | 1.87050 | | 206.15 |
| | 1.48147 | 1.61590 | | 206.13 |
| | | | Av. | 206.17 |

| Sample | | Density of saturated solution $\frac{19.94°}{19.94°}$ | $d\frac{19.94°}{0°}$ |
|---|---|---|---|
| Common lead | | 1.421968 | |
| | | 1.421993 | |
| | | 1.421942 | |
| | Av. | 1.421968 | 1.419475 |
| Cleveite lead | | 1.420439 | |
| | | 1.420422 | |
| | Av. | 1.420431 | 1.417941 |

The saturated solution of common lead nitrate was found to contain 1.522067 gram molecules per liter. The difference in density, 0.001534, corresponds to a difference in atomic weight of 1.01. Hence Pb (cleveite) = 206.17, if common lead is 207.18.

Brennen[26] fractionated lead chloride by the action of Grignard reagent, and metallic lead by crystallization. No difference in the extreme fractions could be detected.

Piutti and Migliacci[27] purified lead tetraphenyl by crystallization from benzene and chloroform. The lead tetraphenyl was then quantitatively converted to bromide by heating in bromine. In this way ordinary lead and lead from Vesuvian cotunnite were compared. The weights are referred to the vacuum standard; C = 12.00; H = 1.008; Br = 79.92.

[25] Gleditsch, Dorenfeldt and Berg, *J. chim. phys.*, **22**, 253 (1925).

[26] Brennen, *Ann. chim. phys.*, [10] **4**, 127; *Compt. rend.*, **180**, 282 (1925).

[27] Piutti and Migliacci, *Gazz. chim. ital.*, **54**, 605 (1924); *Atti accad. Lincei*, [V] **32**, 468 (1923).

ORDINARY LEAD

| Wt. of $Pb(C_6H_5)_4$ | Wt. of $PbBr_2$ | At. wt. of Pb |
|---|---|---|
| 1.79883 | 1.28109 | 207.17 |
| 2.20069 | 1.56732 | 207.19 |
| 2.75962 | 1.96543 | 207.22 |
| 1.77401 | 1.26345 | 207.20 |
| | Av. | 207.19 |

COTUNNITE LEAD

| Wt. of $Pb(C_6H_5)_4$ | Wt. of $PbBr_2$ | At. wt. of Pb |
|---|---|---|
| 1.73653 | 1.23659 | 207.03 |
| 1.46902 | 1.04612 | 207.05 |
| 1.62358 | 1.15621 | 207.08 |
| 1.33592 | 0.95132 | 207.03 |
| 1.43971 | 1.02531 | 207.06 |
| | Av. | 207.05 |

Moles[28] chiefly on the basis of modern gas density determinations computes the following atomic weights: H = 1.00777; Cl = 35.458; Br = 79.918; Ag = 107.882.

Costa[29] by means of an improved form of mass spectrograph has obtained the following results.

$H : H_2 = 1 : 2$
$He : H_2 = 4 : 2.0148$
$He : C = 1 : 3$
$He : Li^6 = 4 : 6.009$
$N : Li^7 = 14.008 : 7.012$

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

# THERMO-ELECTRIC EFFECTS AND THE HEAT CAPACITY OF ELECTRONS IN METALS

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It is the purpose in the first sections of this paper to discuss the nature and proper field of application of the "apparent" heat capacity of electrons in metals, their partial molal heat capacity and the Thomson effect. The final sections comprise a discussion, in the light of experimental facts, of those theories that would identify the apparent heat capacity or the Thomson effect, respectively, with the excess above $3R$ of the atomic heats of metals at high temperatures.

## The Apparent Heat Capacity of Electrons

**Definition.**—This quantity may be adequately defined by considering the total rate of gain of energy of one mole of metal to consist of two parts, associated, respectively, with the changes in motion and positions of the electrons and of the nuclei of the atoms. The absorption due to the nuclei is to be thought of as that which the entire system would show if the elec-

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[28] Moles, *Z. physik. Chem.*, **115**, 61; 117, 157 (1925); *Anal. fís. quim.*, **23**, 39 (1925).

[29] Costa, *Compt. rend.*, **180**, 1661; *Ann. phys.*, **4**, 425 (1925).

trons were rigidly fixed in their positions, at the same time leaving all the conditions affecting the motions of the nuclei themselves exactly as in the actual system. Representing this quantity by $C_N$, the heat capacity (at constant volume) of the mole of metal by $C_V$ and the apparent heat capacity of the electrons as $c$, a defining equation may be written as follows.

$$c = C_V - C_N \tag{1}$$

This conception, since it attempts to "localize" energy which is in part potential and therefore a property of the system as a whole rather than of any part of it, is to that extent artificial. Nevertheless, it fixes uniquely a magnitude; and in spite of the element of the imaginary which makes its direct measurement impossible, it is useful to theories dealing with the internal conditions in metals.

The heat capacity defined above corresponds to one mole of metal but not necessarily to one of electrons. Its conversion to a molal property is complicated by two factors. First, the number of electrons in the metal that are capable of absorbing energy is in general unknown and may vary from metal to metal. In the second place, electrons in different positions or orbits in any one metal (especially of the polyvalent class) may be characterized by different abilities to absorb energy on heating. A kind of average molal heat capacity may, however, be defined by the equation

$$C = c/m \tag{2}$$

In this equation $m$ is the smallest integral number of electrons per atom of metal which is sufficient to account, within the limit of error, for the entire value of $c$.

**Limitation of Magnitude.**—It will be generally agreed that, in systems in which an increase in temperature produces no change in equilibrium positions of any of the electrons, $C$ must lie between zero and $C_V$ in magnitude. Although less obvious, this remains true in the general case also. Any changes involving electron positions may be regarded as shifts in established equilibria. If produced by an increase in temperature these shifts must absorb heat. Heat so absorbed would be included in $C$ as defined above. Even if every other factor involved in $C$ should disappear, this quantity would still remain positive in sign (but obviously could never exceed $C_V$).

## The Partial Molal Heat Capacity of Electrons

**Designation of Electronic Composition.**—The recognition of partial molal quantities[1] for electrons in metals implies that the electronic composition of metals is susceptible of some variation. It is thought that this is the case. To express the composition of these "solutions" the electron is obviously one of the components which should most naturally be chosen.

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[1] For the significance of these quantities in general see Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923.

The singly charged positive metal atom (metal ion) will serve as the other. The composition of the neutral, or uncharged, metal is then expressed as one mole of electrons per mole of metal ion, etc. It is understood, of course, that by any statement of this kind only an average composition is designated and that no implication whatever is intended as to the molecular species that may be present in the metal.

**Definition and Use.**—If $c_v$ denote the heat capacity at constant volume (or correspondingly $c_p$ at constant pressure) of a system consisting of $n_I$ moles of metal ion and $n$ moles of electrons the following equation may be written defining the partial molal heat capacity of the electrons in the system.

$$\bar{C} = (\partial c_v/\partial n)_T \tag{3}$$

It is this quantity which must be used in evaluating thermodynamically the changes with temperature of heat effects attending the isothermal transfer of electrons between any two phases.

**Conditions Affecting $\bar{C}$.**—The differential coefficient in Equation 3 is a function of temperature and of charge. When the non-uniform distribution of electrons in a charged system is considered, it is clear also that $\bar{C}$ (or any other partial quantity) is a function of the shape of the system. It must depend to some extent upon such variables as curvature of surface and ratio of surface to volume. In this respect it differs from the corresponding partial quantity in ordinary solutions, although similar conditions are met in dispersed systems. It is to be noted, however, that the definition assumes nothing as to the distribution of the electrons nor the localization of energy effects in the surface. It includes such surface effects and any others which may be present.

The non-uniformity of composition and, therefore, the shape factors, necessarily disappear only with approach to zero charge or infinite temperature. It is consequently only at sufficiently small charges or sufficiently high temperature that the magnitudes of the partial quantities involving the electron may be considered as properties of the metals. If fairly massive specimens are considered, however, little difficulty is experienced from this source.

**Comparison of Apparent and Partial Heat Capacities.**—$\bar{C}$, unlike $C$, is a real physical quantity, theoretically capable of direct measurement and exact use. In further contrast to $C$, $\bar{C}$ is theoretically in no way limited as to magnitude. Under certain circumstances $\bar{C}$ may be equal to $C$. Under others it may depart from it in either direction. Thus, like any other partial molal quantity, it may be greater or less than the corresponding "actual" or apparent quantity in the solution, may exceed in magnitude the corresponding quantity for the entire solution, or may have zero or negative values. It is perhaps worth while to consider conditions leading to some of these results.

The condition for the realization of equality between $\overline{C}$ and $C$ is that a small change in ratio of electrons to metal ions shall produce no corresponding variation in molecular species or constraints in the system.[2] The nature of metallic systems, however, is not such as to lead to the belief that this condition is often fulfilled. Any change in electronic composition of the metal is likely either to cause a shift in some equilibrium between the various molecular species in the metal or to change the intensity of the constraints between them. It is desired here to illustrate in a qualitative way the second of these contingencies. This is done in Fig. 1. In this figure $C_N$ and $c$ are represented at a given temperature before the introduction of extra electrons in a hypothetical case. It is assumed that the added electrons increase the constraints throughout the metal. The effect of such a tightening would be to shift the specific-heat curves to the right. The dotted curves may therefore be assumed to represent those corresponding to the original system but with the constraints (and nothing else) changed. The heat capacity that the original number of electrons would have in the new state is indicated by $c'$ in the figure. Neglecting the small change in $C_N$, the change produced in $C_V$ by the addition of the electrons is equal to the change, $c' - c$, in $c$. If the latter change is numerically less than the heat capacity of the added electrons in the new state, $\overline{C}$ is less than $C$, but is positive in sign. If the decrease, $c' - c$, is numerically equal to or greater than the heat capacity of the added electrons, $\overline{C}$ is zero or actually negative, although $C$ itself has

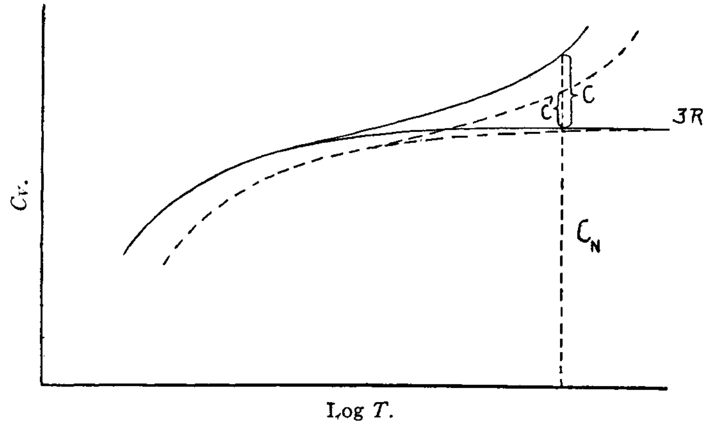

Fig. 1.

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[2] There is a further condition requiring that the transferred electrons be able to enter or leave all positions in the system in which electrons may contribute appreciably to the energy absorption. This condition is probably fulfilled in the neutral metals of simple type—possibly in all neutral metals. It may not always be met in charged metals, because the added electrons may go largely to the surface, where their energy absorption may differ from that in the interior.

a large positive value. In this deduction, had the opposite effect in constraints been assumed, $\bar{C}$ would have been found greater than $C$. In the absence of any information regarding the actual interactions in metals, there is no reason to anticipate one of the above relations more than another.[3]

## The Thomson Effect

**Definition.**—There are many conventions in use concerning the Thomson effect. Here the term will be used to denote the heat absorbed by a system consisting of a metal in which a temperature gradient exists when electrons in the metal are transferred *reversibly*[4] from a temperature $T$ to a higher temperature $T + \mathrm{d}T$, the effect being expressed per mole of electrons transferred and per degree difference in temperature. It is therefore a measure of the entropy change (of the system) attending the process indicated. This entropy change is the difference in partial molal entropy of electrons at $T$, and $T + \mathrm{d}T$, in the metal in which the temperature gradient exists. Representing the Thomson effect by $\sigma$ and the partial molal entropy of electrons by $\bar{S}$, the following defining equation may therefore be written.

$$\sigma\,\mathrm{d}T = T\mathrm{d}\bar{S} \tag{4}$$

In evaluating $\mathrm{d}\bar{S}$, it is necessary to consider not only the temperature gradient, but the gradient in electronic composition which must normally accompany it. In the case of ordinary solutions the latter is called the Soret effect. In metals it is made manifest by the charges developed at the ends of conductors in which there is a temperature gradient. Denoting the composition variable by $N$, the entropy change (normally at constant pressure) attending the process under consideration may be written

$$\mathrm{d}\bar{S} = (\partial\bar{S}/\partial T)_{N,P}\,\mathrm{d}T + (\partial\bar{S}/\partial N)_{P,T}\,\mathrm{d}N \tag{5}$$

The coefficient $(\partial\bar{S}/\partial T)$ in this equation is equal to $\bar{C}/T$. The coefficient $(\partial\bar{S}/\partial N)$ in the last term, however, is a known function only for

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[3] The above discussion is based on the assumption that added electrons distribute themselves throughout the metal. Whenever the charge is sufficiently high to cause changes in charge to be restricted primarily to the surface layers, the interactions imagined above between the atoms and electrons must also be restricted mainly to surface effects (proportionately more intense than the volume effects), but no essential feature of the discussion is changed by this.

[4] The reversible transfer referred to implies the movement of an infinitesimal charge under equilibrium conditions, for example, in a thermocouple balanced by a closely equal and opposite e.m.f. When a small charge is carried under such conditions from one end to the other of a wire of finite extent, the process may be regarded as the movement of the same charge along the wire, into and out of each element of length, or as a small displacement of all electrons in the wire, certain electrons entering any given segment and remaining there and others leaving in a later interval. Exactly the same series of changes occurs in the conductor in either case and any attempt to explain the thermal changes in terms of the electrical must resolve this motion into successive actual transfers of the kind considered above.

solutions whose internal conditions do not change appreciably as $N$ is changed. Moreover, the variation in composition due to the temperature gradient is itself characteristic of the metal employed, and not calculable thermodynamically.[5] In the absence of specific information concerning these factors, the defining equation for $\sigma$ may best be left in the form resulting from combination of (4) and (5).

$$\sigma = \overline{C} + (\partial\overline{S}/\partial N)_{P,T}\, \mathrm{d}N/\mathrm{d}\ln T \tag{6}$$

**Comparison of Thomson Effect and Partial Molal Heat Capacity.**—Since the last term of Equation 6 is not often likely to be exactly zero, $\sigma$ is seldom exactly equal to $\overline{C}$. It follows, therefore, that in a strict sense $\sigma$ is applicable only in the treatment of phenomena involving a temperature gradient, and its use in any other connection is theoretically unjustifiable. Practically, it is probable that the term in the expression for $\sigma$ arising from the entropy of transfer of electrons between regions of metal of different charge is usually small compared to $\overline{C}$. Whether it is so small as to be negligible in every application which may be made is a question concerning which there is at present no evidence.

**Significance of Directly Measured Thomson Effects.**—The methods of direct determination of the Thomson effect necessarily utilize finite currents. The condition of reversibility of transfer of electrons which applied to the definition above is therefore not fulfilled. A further point of difference is that with finite currents the transfer of electrons between regions of differential temperature difference affects the charge of the metal in these regions in a different way than in the reversible transfer. A certain overlapping, which owing to the atomic nature of electricity will be complete only in infinitely large currents, of the charges entering and leaving any small region may result in smaller changes in relative charge of the metal in these regions than in the reversible transfer. Nevertheless, except at infinite currents, these smaller differences in charge will be created and exist in adjacent segments for very small intervals of time. If the physical reactions to the changes in charge are sufficiently rapid, the heat effects will be partly due to them and the measured quantity will partake somewhat of the nature of the partial quantities. The values of these coefficients obtained with finite currents therefore, while they cannot be the same as the reversible effects, may be approximately so. There are two indications that these effects are in fact parallel. First, the Peltier heats, which are analogous quantities, are roughly the same measured directly as calculated from the e.m.f.'s of thermocouples. Second, the direct values of the Thomson coefficients for different metals are roughly in the order that would be obtained from thermocouples under reversible conditions. In the following work the assumption of approximate equality of reversible and irreversible effects will be made use of to the extent that the sign of the

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[5] The Soret effect will be discussed in another paper.

direct quantity, where this can be ascertained experimentally, is considered to be the same as that of the reversible effect.

**Effects at Constant Volume and Constant Pressure.**—The Thomson effects of practical interest all correspond to conditions of constant pressure. To calculate the effects at constant volume, knowledge of the change in volume with charge, among other data, would be required. This knowledge is wholly lacking. The considerations of the following section will be noted to involve this unavoidable discrepancy.

## The Excess Specific Heat of Metals and the Thomson Effect

The foregoing analyses offer a basis for the comparison and discussion of the theories mentioned in the introduction which would connect the apparent specific heat or the Thomson effect, respectively, with the excess above the normal value of the heat capacities of metals. These theories may be represented in essence in the form of equations in which $C_R$ denotes the heat capacity according to the "normal curve," and the remaining quantities have the same significance as in the preceding sections, as follows.

$$(C_V - C_R)/m = C \tag{7}$$

and

$$(C_V - C_R)/m = \sigma \tag{8}$$

The history of the hypothesis expressed by (7) and a full discussion of the evidence bearing upon it will be found in a former paper.[6] Here it will only be recalled that the equation is approximate in character and not necessarily valid for all metals or under all conditions. In no case is it susceptible of proof or disproof. In spite of this, the inference that it is often true is rather strongly supported. Its underlying hypothesis is plausible in view of the independent evidence concerning the looseness of constraint of electrons in metals, and the known effects of such looseness in other cases. There is no single fact known which is directly opposed to the idea and there are a number that favor it. Thus $C_V - C_R$ experimentally is always positive in sign, in agreement with the deduction in the first section concerning $C$. Perhaps the strongest supporting evidence, however, consists in the correspondence which may be traced[6] between the magnitude of $C_V - C_R$ and the electropositive character of the different metals.

Equation 8 is of interest because of its bearing upon the conditions existing in metals. In the obvious absence of any necessary relation between the quantities in the equation, the simplest explanation of any general equality which might be found would be that the conditions under which $\sigma$ might be closely equal to $\overline{C}$ and the latter to $C$ were fulfilled in the metals concerned. Even more valuable than this qualitative knowledge would be the ready methods of interdetermination of these thermo-

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[6] Eastman, Williams and Young, THIS JOURNAL, **46**, 1184 (1924).

dynamically useful quantities and $C_V$ which would be made available. It is of some importance therefore to make the most general examination possible of (8). The validity, in so far as order of magnitude is concerned, has already been shown for a number of metals in an interesting investigation by Latimer.[7] The present purpose is to make the more exacting and comprehensive tests of the equation which are now possible. Familiarity with Latimer's methods and results will be assumed in the discussion.

It may be noted at the outset that the data now available make it clear that several of the apparent discrepancies pointed out by Latimer are real. Of these perhaps the most important is in the data relating to calcium. It has been established in experiments by A. M. Williams and T. F. Young[8] that the original data of Swisher[9] on the thermal e.m.f. of this metal are correct as to sign. When these data are used to calculate "entropy" differences between 100° and 400° a value of 0.04 cal./deg. is found, while from the specific heats of Ref. 6 the resulting value is 0.55. And if the specific-heat curves at low temperatures are used to calculate the e.m.f. of the calcium-magnesium couple the result is incorrect in sign.

The interpretation of the results of the other comparisons offered by Latimer is rendered difficult by three factors in them which may tend to obscure differences in the quantities compared. In the first place, although the desired comparison is between $\sigma$ and $(C_V - C_R)$ for the given metals, the actual comparison is between differences in these quantities in various pairs of metals. Secondly, these differences are not directly compared at any one temperature (except in Figs. 5 and 3 of Ref. 7, the latter of which is, however, based upon less reliable specific heats than are now available) but only as averages over a considerable interval in log $T$. Third, in many instances the value of $m$, which is necessary for a significant comparison, is quite unknown.

The second and third of these difficulties are avoided in the comparisons exhibited in Table I below. The data for the alkali metals there presented are very damaging to the claims of Equation 8 as applied to this group. Because of the simple type of the metals in it the discrepancies are weighty ones.

TABLE I

COMPARISONS OF DIFFERENCES IN THOMSON EFFECTS AND EXCESS HEAT CAPACITIES OF THE ALKALI METALS AGAINST SILVER AT 0°C.

| Metal | Li | Na | K | Rb | Cs |
|---|---|---|---|---|---|
| $\Delta\sigma$ cal./deg. | −0.35 | 0.077 | 0.21 | 0.24 | −0.035 |
| $\Delta C$ cal./deg. | .... | .41 | .9 | (1.2) | (1.5) |

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[7] Latimer, THIS JOURNAL, **44**, 2136 (1922).

[8] The author is indebted to Drs. Williams and Young not only for these experiments but also for assistance in development of the ideas of this paper through numerous discussions.

[9] Swisher, *Phys. Rev.*, [2] **10**, 601 (1917).

In this table $\Delta\sigma$ is written for the difference, $(\sigma - \sigma_{Ag})$ in Thomson effects of the metals as compared with that of silver. The values are obtained from the slopes (determined graphically) of Bidwell's e.m.f.—temperature curves[10] together with the slope of the platinum-silver couple from Fig. 2 of Ref. 7. $\Delta C$ represents differences, $(C_V - C_R) - (C_V - C_R)_{Ag}$, in their excess specific heats. The last quantities are obtained from Ref. 6 for sodium and potassium. Those for rubidium and cesium are obtained approximately by adjustment of Rengade's measurements [*Compt. rend.*, **56**, 1879 (1913)], assuming that his values differ from the "best values" by the same amount that his result for potassium differs from the value chosen in Ref. 6 as most representative. No value of $C_R$ for lithium at 0° is known at present, so no value of $\Delta C$ may be given for it at this temperature. The indication is that its magnitude is considerable, however, since $C_V$ apparently exceeds $3R$ markedly at somewhat higher temperatures.

To show that elimination of the second of the above factors is alone enough to remove some of the metals from the list for which (8) may be valid, Table II has been constructed. Nickel, the metal referred to in it, is chosen merely as an illustrative example. Similar figures for cobalt between 200° and 450° show a less marked but unmistakable tendency to diverge, while iron between 200° and 700° shows a more extreme discrepancy than nickel. Other metals showing similar though less pronounced deviations are aluminum, tungsten and molybdenum.

TABLE II

COMPARISON OF DIFFERENCES IN THOMSON EFFECTS AND EXCESS HEAT CAPACITIES OF NICKEL AGAINST SILVER AT VARIOUS TEMPERATURES

| *t*, °C. | 0 | 100 | 200 | 300 |
|---|---|---|---|---|
| $\Delta\sigma$, cal./deg. | 0.39 | 0.41 | 0.0 | −0.68 |
| $\Delta C$, cal./deg. | .2 | .8 | 1.3 | 1.7 |

The symbols in this table have the same meaning as in Table I. The values of $\Delta\sigma$ were obtained graphically from the e.m.f. data in Fig. 2 of Ref. 7, and the specific-heat data from Ref. 6.

The necessity of considering only *differences* in the quantities for two metals when testing Equation 8 is partially obviated by the direct determinations of $\sigma$ in individual metals which are available. These measurements are unfortunately of such limited accuracy as to be unsuitable for numerical comparison. Nevertheless, important information may be obtained from them in certain cases. Thus, it is clearly established that under the conditions of measurement (previously discussed) $\sigma$ is negative in sign for a number of metals.[11] The list includes copper, silver, gold, zinc and cadmium. (Indirect determinations from e.m.f. data apparently place lithium, cesium, molybdenum and tungsten in this group, as well as sodium, iron and nickel at certain temperatures.) The temperatures

[10] Bidwell, *Phys. Rev.*, **23**, 357 (1924).

[11] See, for example, Lecher, *Ann. Phys.*, [4] **19**, 853 (1906). Berg, *ibid.*, [4] **32**, 477 (1910). Cermak, *ibid.*, [4] **33**, 1195 (1910). Borelius and Gunneson, *ibid.*, **65**, 520 (1921).

over which these negative effects have been directly investigated extend in some cases as high as 500°. The data indicate that over these ranges in most of the cases cited above the effect remains negative in sign and increases numerically as the temperature is increased. Over considerable portions of the same temperature intervals $C_V - C_R$ is small for some of these metals. It is, however, beyond experimental error and always positive.

It will be noted that most of the metals having transition points show negative values of $\sigma$. Exceptions to this behavior may be cited, and a number of metals in which $\sigma$ is negative do not have transitions.[12] It seems obvious that the approach to the transition temperature may be accompanied by conditions which cause $C$, $\bar{C}$ and $\sigma$ to diverge from one another. It introduces, however, nothing that is different in character from the general conditions discussed in the first sections, and nothing that may not be met in any metal, with or without transitions. There is of course the possibility in these cases that $C$ as obtained from specific heats in the immediate neighborhood of an inversion is larger than the true value. This does not affect the conclusion as to its inequality with $\sigma$ when the latter is negative in sign.

## Conclusions

Consideration of the data presented in the preceding reveals evidence for nearly all of the numerous metals studied that is fundamentally unfavorable to the view that $\sigma$ and $C$ are almost equal. The effects of the influences which render them unequal are far from negligible as compared with the magnitude of either quantity itself. Unfortunately, therefore, $C$ and $C_V$ cannot be calculated from thermo-electric data. As pointed out previously, $\bar{C}$ cannot be assumed to be identical with $\sigma$ unless the Soret phenomenon is without significant effect upon it. If this rather likely assumption is made, however, certain interesting inferences may be drawn from comparison of the relative magnitudes of $\bar{C}$ and $C$. In the alkali metals and in silver, gold, zinc, calcium and cadmium $\sigma$ and, therefore, $\bar{C}$ are smaller than $C$; in magnesium the two are apparently nearly equal; while in aluminum, lead and platinum, if $m$ may be assumed to be greater than 1, $\bar{C}$ is greater than $C$. Interpreting these differences in the light of the earlier discussion, it may be said that in the first of these groups an increase in the ratio of electrons to atoms increases the constraints in them. In magnesium there is little effect, while in the last group the constraints appear to be de-

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[12] Bidwell, Ref. 10, attributed inversions to the alkali metals because of the marked variations in slope which occur at certain temperatures in the resistance and e.m.f.—temperature curves. From the experimental points, however, the changes appear to be continuous. If they are so in fact they do not necessitate the assumption of two forms of the metal. Further evidence is required before the existence of allotropic modifications is established.

creased.[13] The predominating effect seems, therefore, to be a "tightening." The suggestion occurs in explanation that possibly the extra electrons when introduced in most cases tend to enter with the other electrons into stable groups or configurations which could not be formed to the same extent without them.

## Summary

The apparent heat capacity of electrons, their partial molal heat capacity and the Thomson effect are defined and compared, and the conditions under which they might be numerically equal discussed. The available evidence is examined to determine whether such equality exists in actual cases. It is concluded that for a large majority of the metals studied the apparent heat capacity is not nearly equal to the Thomson effect, and probably not to the partial molal heat capacity. From comparisons of the magnitude of the last quantity with the first, certain tentative conclusions are drawn relating to the specific effects upon interatomic constraints of increasing the negative charge of metals.

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# THE ACCURATE MEASUREMENT OF HEATS OF VAPORIZATION OF LIQUIDS

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That the accurate measurement of heats of vaporization is one of considerable difficulty, is evident from the widely divergent values found in the tables of physical constants. The methods available may be divided into two general classes: (1) condensation methods and (2) evaporation methods.

·One great difficulty with the condensation method is the correction required for the heat given out by the condensed liquid cooling from the boiling temperature (temperature of condensation in the calorimeter) to the temperature of the calorimeter. This correction involves an accurate knowledge of the specific heats of the liquids used over this range of temperature and such data are no more accurately known than the heats of evaporation which are being measured. The direct evaporation methods, which do not involve such a correction, have a distinct advantage in this respect. Also, since electrical quantities are susceptible of very accurate measurement, the direct method seems preferable. Another great

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[13] Whether these assumed reactions occur entirely in the surface regions of the metals or in the interior is not important from the present standpoint.

It should be noted also that other languages, including that of the quantum theory, may be used in describing these results.