

cal./mole. The probable error resulting from these corrections is difficult to estimate, but may be as high as 200 cal.

Entropy of Solution of Lithium Carbonate.—Seyler and Lloyd³ measured the solubility of lithium carbonate at 298.1°K., in water solutions containing various amounts of carbon dioxide. They measured the total carbonate and bicarbonate by titration. By plotting the reciprocal of the mean molality of lithium ion and carbonate ion against the square root of the ionic strength, a fairly good straight line was obtained, from which the activity coefficient of lithium carbonate at saturation was found to be 0.59. The calculation is not of high accuracy but fortunately this does not affect greatly the free energy of solution. For example, a change of 10% in the activity coefficient would change the free energy of solution only about 180 cal., which corresponds to 0.3 E. U. in the entropy of lithium ion. The solubility of lithium carbonate in pure water is 0.169 *M* according to the same authors, so that $\Delta F^\circ = 3280$ cal./mole.

The entropy change when the solid salt dissolves to form a hypothetical one molal solution is given by the expression

$$\Delta S^\circ = (\Delta H - \Delta F^\circ)/T =$$

$$(-4200 - 3280)/298.1 = -25.1 \text{ E. U.}$$

(3) Seyler and Lloyd, *J. Chem. Soc.*, 111, 994 (1917).

Entropy of Lithium Ion.—The entropy of carbonate ion⁴ is -12.7 E. U., so that the entropy of lithium ion is given by the expression

$$S^\circ_{\text{Li}^+} = \frac{1}{2}(\Delta S^\circ + S^\circ_{\text{Li}_2\text{CO}_3} - S^\circ_{\text{CO}_3^{--}}) =$$

$$\frac{1}{2}(-25.1 + 21.6 + 12.7) = 4.6 \text{ E. U.}$$

Because of the absence of calorimetric data on lithium compounds, the entropy of lithium ion previously has been calculated from the entropy change of the lithium electrode reaction, even though the uncertainties were quite large.⁵ The value thus obtained (-1.8 E. U.) differs by 6.4 E. U., or about 1900 calories, from the value calculated above. Since we believe the possible uncertainty introduced into the entropy of solution of lithium carbonate by the troublesome corrections for hydrolysis are not greater than one E. U. in $S^\circ_{\text{Li}^+}$, we must conclude that the discrepancy is due to errors in the entropy change of the electrode reaction.

Summary

The heat capacity of lithium carbonate has been measured from 16 to 300°K. The entropy of lithium carbonate at 298.1°K. obtained from these data is 21.60 E. U. The heat of solution in water at 298.1°K. has been determined. The entropy of lithium ion calculated from these and other data has been found to be 4.6 E. U.

(4) Latimer, Schutz and Hicks, *J. Chem. Phys.*, 2, 82 (1934).

(5) Latimer, *Chem. Rev.*, 18, 351 (1936).

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RECEIVED SEPTEMBER 8, 1936

[CONTRIBUTION FROM VALENCIA HIGH SCHOOL]

The Boyle Temperature and a General Equation of State

BY GEORGE WOOLSEY

If a general equation of state is possible the Boyle temperature, the temperature at which $\left(\frac{\partial PV}{\partial P}\right)_T = 0$, at zero pressure must be either the same temperature or a function of $RT_c/p_c v_c$ (n in my notation) for all pure non-associating and non-dissociating substances. Empirically the older data seem to indicate that the Boyle temperature, T_B (reduced), is a function of n . For example, taking T_B as the temperature for which the second virial coefficient equals zero, Holborn and Otto¹ found

Substance	Ne	He	H ₂	O ₂	A	N ₂
T_B	3.00	3.65	3.21	2.72	2.73	2.56
n	3.254	3.261	3.282	3.423	3.424	3.428

(1) Holborn and Otto, *Z. Physik*, 33, 9 (1925); 33, 365 (1926).

Recomputing the values for oxygen and argon, using more recent values for critical temperatures, gives 2.74 and 2.72, respectively. These figures seem to indicate quite definitely that T_B is a function of n .

However, using data compiled by Beattie and Bridgeman,² approximate values of T_B are obtained which indicate that the other possibility, that T_B is a constant, is the correct one.

Substance	Ne	H ₂	O ₂	A	N ₂	CH ₄
T_B	<2.77	Between 3.7 and 2.5	>2.4	2.5	Between 2.56 and 2.33	2.48
n	3.245	3.282	3.423	3.424	3.428	3.448

(2) Beattie and Bridgeman, "A New Equation of State for Fluids," *Proc. Am. Acad. Arts Sci.*, 63, No. 5 (1928).

An additional value is found from the work of Bartlett, *et al.*, THIS JOURNAL, 52, 1363-1374 (1930).

Substance	CO
T_B	Between 2.78 and 2.41
n	3.404

These data indicate that the value $T_B = 2.5$ for all of these substances is very nearly correct. The use of this relationship, $T_B = 2.5$, enables the constants of the equation³

$$PV + \frac{AV - AB}{T^2V^2 + CT^3V + DT^4} = nT + (B + K)P + q \log(P + 1)/T^w$$

to be determined in a way which is much more

1	1	0.386691 ($C^2 - 17.3125C + 8.078125 - D$)
0	1.5	.643843 ($C^2 - 5.125C + 5.03125 - D$)
0.5	1.5	.407191 ($C^2 - 9.8467C + 6.21168 - D$)
1	1.5	.257535 ($C^2 - 17.3125C + 8.078125 - D$)

Work with $w = 0$ or 0.5 is found to lead to unusable results.

The constants for the equation of state are determined for the various values of x , w and q from this table by substituting $V = 0.36$ at $P = 20$ and $V = 0.4$ at $P = 10$, with $T = 1$ for both, and solving the resulting simultaneous equations for C and D . These values are then checked at three points on the critical isotherm as indicated.

x	w	C	D	q	$(B + K)$	A	$-AB$
0	1	0.9237	2.4824	1.2875	0.2861	4.1419	8.7402
0.5	1	.8390	0.2943	1.0027	.2871	5.9266	0.1298
1	1	.9859	-4.1268	1.5046	.2829	11.0564	-17.4489
0	1.5	.9298	+3.1629	1.3085	.2859	3.4910	+11.4296
0.5	1.5	.8973	1.1216	1.1972	.2869	5.3753	3.3713
1	1.5	1.0210	-2.2272	1.6299	.2804	9.3327	-9.9556
		P (calcd.) at $\begin{cases} P \text{ exp.} \\ V \\ T \end{cases}$		0.5	5	2	
				5.2 ^a	0.454	0.55	
				1	1	1	
x	w			0.544	4.9	1.85	
0	1			.499	4.95	2.00	
0.5	1			.417	8.24	Impossible	
1	1			.539	4.86	1.78	
0	1.5			.511	4.94	1.94	
0.5	1.5			.455	12.5	Impossible	
1	1.5						

^a Additional data obtained since the preceding paper³ indicate that $V = 5.2$ at $P = 0.5$ is a better value than the previously used $V = 5.4$.

convenient than that used before. (The equation as given here contains the expression T^w which was not previously used. Work with the equation indicates that the logarithmic term should be an inverse function of the temperature.)

To make use of the above relationship the equation is divided by T and the expression for $(\partial PV/T/\partial P)_T$ is obtained by differentiation and set equal to zero at $P = 0$ when $T = T_B$. Two substitutions, $PV = nT$ when $P = 0$ and $dV/dP = T/P(\partial PV/T/\partial P)_T - V/P$ are used to obtain the final expression. This is

$$q = 2.30259 T_B^w \{A/nT_B^{(x+1)} - (B + K)\}$$

Letting $n = n_0 = 3.25$, $T_B = 2.5$, $A = C^2 + 3C + 3 - D$ and $B + K = C + 3 - n - 0.30103 q$, the following expressions for q are found for various values of x and w .

x	w	$-q$
0	1	0.966720 ($C^2 - 5.125C + 5.03125 - D$)
0.5	1	.61140 ($C^2 - 9.8467C + 6.21168 - D$)

(3) Woolsey, THIS JOURNAL, 58, 984-987 (1936).

This table shows that $x = 0.5$ is a much better value than $x = 0$ or $x = 1$. A point in the liquid phase in equilibrium with the vapor, $T = 0.85$, $P = 0.3745$ and $V = 0.49048$, is used to determine one relation between y and z . When these values are substituted in the equation of state the equations $0.85^y + 0.7152 \times 0.85^z = 2.0509$ when $w = 1$ and $0.85^y + 2.5484 \times 0.85^z = 4.2074$ when $w = 1.5$ are obtained. Another relation between y and z is obtained by making use of the fact that for $V = 1$ the $(AV - AB)/(T^{1/2}V^2 + CT^3V + DT^4)$ term must be a maximum at the critical temperature. Differentiating the denominator with respect to T and setting it equal to zero gives the relation $0.5 + yC + zD = 0$. Solving these two equations in y and z gives $y = 0.333$ and $z = -2.67$ when $w = 1$; and $y = 1.8$ and $z = -1.88$ when $w = 1.5$. The table below shows that the values with $w = 1.5$ give the better solution.

<i>T</i>	8	8	4	4	0.85	0.85
<i>V</i>	1.56	2.80	0.91	1.54	5.8264	.49048
<i>P</i> (calculated) (<i>w</i> = 1)	19.77	10.15	18.3	9.50	0.355	(.373)
<i>P</i> (calculated) (<i>w</i> = 1.5)	20.34	10.31	20.04	10.07	.366	(.379)
<i>P</i> (experimental)	20	10	20	10	.3745	.3745 ^a

* Used to obtain the relation between *y* and *z*.

The use, then, of the Boyle temperature has resulted in a modification of the form of the general equation of state by showing that the logarithmic term is a function of *T* and it has simplified considerably the determination of the constants of the equation. Using the critical point, the ideal gas value at low pressure, two points on the critical isotherm at high pressure, the Boyle temperature,

one point in the liquid phase and the second term maximum at the critical point, an equation

$$PV + \frac{5.3752V + 3.3713}{T^{0.5}V^2 + 0.8973T^{1.8}V + 1.1216T^{-1.88}} = \frac{3.25T + 0.2869P + 1.1972T^{-1.5}\log(P + 1)}{}$$

is found which fits fairly closely at the eight other widely divergent points which were tested.

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RECEIVED JUNE 23, 1936

[CONTRIBUTION FROM THE DIVISION OF PLANT NUTRITION, UNIVERSITY OF CALIFORNIA]

Age and the Chemical Composition of White Fir Wood

BY IRVING H. ISENBERG

The effect of age on the chemical composition of wood has been studied by few investigators. The composition of sapwood and heartwood has been compared,¹⁻⁴ separate trees examined^{4,5} or a single constituent determined in one tree.^{6,7} It would seem that differences due to age may be studied best by demarking zones of various ages on a cross-section from a definite height in a selected tree, in order to eliminate environmental factors as far as possible. The material should be examined for all important constituents.

Selection of Material

In the past, little effort has been made to record data on the environment in which the wood to be analyzed was grown. Since there is a possibility that environment and chemical composition may be correlated, such data may be of value in the future.

The wood used for this study was obtained from a white fir tree (*Abies concolor*) growing in a mixed conifer stand near Quincy, California. It was a healthy tree, approximately 100 feet tall and 185 years old. The diameter, breast high, was 23 inches (58 cm.). Classed as a dominant number three,⁸ it had a long, pointed crown of medium width. The site was such that a tree dominant

throughout its life had an average height of 125 feet (38 meters) at 300 years of age; the elevation 3900 feet (1150 meters); the slope 50%; and the exposure northwesterly. The average annual precipitation is 35 to 40 inches (89 to 101 cm.), with little during the summer season.

Preparation of Material

A section 7 inches (17.8 cm.) thick and 17 inches (43 cm.) in diameter, without the bark, was sawed from the white fir tree described above, at a point 12 feet (3.66 m.) above the ground level. The age at this point was one hundred and sixty years. This cross-section was carefully marked, following the 15th, 40th, 85th and 125th annual ring from the periphery, thus dividing the piece into five bands or zones. These zones were chiseled to sticks approximately 0.2 × 0.2 × 3.5 inches (0.51 × 0.51 × 8.9 cm.) and after drying at room temperature, chopped in a Wiley mill until all the sawdust passed a 60-mesh screen. In common with standard procedure, all sawdust passing an 80-mesh screen was discarded. Knots and compression wood areas were eliminated.

Data concerning these zones are listed in Table I. The total (T) was mixed from weighted proportions of the zones. The wood was 65.4% sapwood and 34.6% heartwood. The average apparent specific gravity of the sapwood was 0.425 and of the heartwood 0.440.

TABLE I
MEASUREMENTS ON AGE ZONES

No. of rings from periphery	Sym- bol	Sap- or heart- wood	Radial width of zone, in.	Area of zone, sq. in.	% of total	% of sap- or heart- wood
1-15	A	S	0.5	23.0	10.1	15.5
16-40	B	S	1.25	60.6	26.8	40.9
41-85	C	S	1.75	64.6	28.5	43.6
86-125	D	H	2.38	57.0	25.1	72.5
126-160	E	H	2.62	21.6	9.5	27.5
1-160	T	..	8.50	226.8	100.0	..

- (1) E. Gäumann, *Flora*, **23**, 344 (1928).
- (2) G. J. Ritter and L. C. Fleck, *Ind. Eng. Chem.*, **15**, 1055 (1923).
- (3) G. J. Ritter and L. C. Fleck, *ibid.*, **18**, 576 (1926).
- (4) C. G. Schwalbe and E. Becker, *Z. angew. Chem.*, **33**, 14 (1920).
- (5) P. Klason, *Cellulosechem.*, **12**, 36 (1931).
- (6) G. De Chalmot, *Am. Chem. J.*, **16**, 611 (1894).
- (7) B. Johnsen and R. W. Hovey, *J. Soc. Chem. Ind.*, **37**, 132T (1918).
- (8) D. Dunning, *J. Agric. Research*, **36**, 755 (1928).