Heat Capacities of Aqueous NaCl, KCl, MgCl₂, MgSO₄, and Na₂SO₄ Solutions Between 80° and 200°C

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By use of the bomb calorimeter previously used for seawater solutions by Bromley et al., the heat capacities at saturation (saturated vapor pressure) of several salt solutions to 12% by weight have been measured. From the smoothed results the values of the heat capacity at constant pressure have been calculated. A limited number of apparent and partial (unit mass) heat capacities are also presented. Values of relative enthalpies for NaCl solutions are given and found to compare favorably with literature data.

The salts chosen for this investigation were those which, when taken in the proper proportions, make up the major constituents of seawater. The equipment, basic theory, and procedure have been described by Bromley et al. (1) and recorded in detail by Likke (3). All heat capacities are in defined calories (4.1840 J) per gram per $^{\circ}C$.

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Table I. Experimental Heat Capacities

tion were those mass fraction of salt. For the apparent and partial quanbritions, make up titles the extended Debye-Hückel theory is used as follows: ribed by Bromley

Theory

are summarized below.

$$\frac{\sigma(|1/2)}{3} = \overline{C_{P(s)}}^{\circ} + \frac{\nu}{2} |Z_{+}Z_{-}|^{1/2} \left[\frac{1}{1+1^{1/2}} - \frac{\sigma(|1/2)}{3} \right] \frac{A_{j}}{M_{s}} - Bm + \dots \quad (3)$$

The equations relating the various quantities reported

 $C_P = C_{\text{sat}} + T \left(\frac{\partial u}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_{\text{sat}}$

 $C_P = C_{P(w)}^{+} (1 - x) + x(\phi C_{P(s)} = \overline{C_P(w)}^{+} (1 - x) + x\overline{C_P(s)}^{+}$

All values are reported on a mass basis. Thus x is the

(1)

| | | | | Sodium | Chloride So | olutions | | | | | |
|-------|---|------|--------|--------|-------------|----------------------------|----------|--------|--------|--|--|
| | At Thermal Saturation (C _{sat}) | | | | | | | | | | |
| Wt% | 80°C | 90°C | 100°C | 120°C | 130°C | 140°C | 160°C | 180°C | 200°C | | |
| 1.986 | 0.9792 | | 0.9836 | 0.9893 | | 0.9959 | 1.0063 | 1.0188 | 1.0355 | | |
| 3.32 | 0.9646 | | 0.9686 | 0.9728 | | 0.9795 | 0.9886 | 0.9997 | 1.0147 | | |
| 4.98 | 0.9478 | | 0.9504 | 0.9538 | | 0.9599 | 0.9681 | 0.9783 | 0.9908 | | |
| 8.41 | 0.9108 | | 0.9142 | 0.9161 | | 0.9206 | 0.9270 | 0.9350 | 0.9451 | | |
| 1.09 | 0.8879 | | 0.8890 | 0.8913 | | 0.8948 | 0.8997 | 0.9053 | 0.9141 | | |
| | ···· | | | At | Constant Pr | essure (C _P) | | | | | |
| 1.986 | 0.9793 | | 0.9838 | 0.9898 | | 0.9969 | 1.0081 | 1.0220 | 1.0384 | | |
| 3.32 | 0.9647 | | 0.9688 | 0.9733 | | 0.9804 | 0.9903 | 1.0028 | 1.0199 | | |
| 4.98 | 0.9479 | | 0.9506 | 0.9543 | | 0.9608 | 0.9698 | 0.9812 | 0.9956 | | |
| 8.41 | 0.9109 | | 0.9144 | 0.9165 | | 0.9214 | 0.9284 | 0.9375 | 0.9492 | | |
| 1.09 | 0.8880 | | 0.8892 | 0.8917 | | 0.8955 | 0.9010 | 0.9075 | 0.9179 | | |
| | | | × | Pota | ssium Chlor | ide Solutions | i | | | | |
| | | | | At T | hermal Satu | ration (C _{sat}) | <u> </u> | | | | |
| 2.054 | 0.9776 | | 0.9813 | 0.9865 | | 0.9946 | 1.0049 | 1.0187 | 1.0362 | | |
| 4.098 | 0.9539 | | 0.9584 | 0.9624 | | 0.9698 | 0.9787 | 0.9906 | 1.0051 | | |
| 6.072 | 0.9307 | | 0.9343 | 0.9394 | | 0.9459 | 0.9543 | 0.9654 | 0.9767 | | |
| 8.148 | 0.9088 | | 0.9130 | 0.9182 | | 0.9233 | 0.9314 | 0.9403 | 0.9527 | | |
| 0.111 | 0.8847 | | 0.8890 | 0.8935 | | 0.8986 | 0.9055 | 0.9135 | 0.9243 | | |

(Defined cal/g °C)

| | | | | (Defined | cal/g °C) | | | | |
|--|--|---------------------------------------|--|---|----------------------------|--------------------------------------|--|--|-------------|
| | | - | Po | tassium Chl | oride Solutio | ns | | | |
| | | | | At Constant | Pressure (C _P | ·) | | | |
| .054 | 0.9777 | | 0.9815 | 0.9870 | | 0.9956 | 1.0067、 | 1.0219 | 1.0416 |
| .098 | 0.9540 | | 0.9586 | 0.9629 | | 0.9707 | 0.9804 | 0.9936 | 1.0101 |
| 072 | 0.9308 | | 0.9345 | 0.9398 | | 0.9467 | 0.9559 | 0.9682 | 0.9813 |
| 148 | 0.9089 | | 0.9132 | 0.9186 | | 0.9241 | 0.9328 | 0.9428 | 0.9569 |
| .111 | 0.8848 | | 0.8892 | 0.8939 | | 0.8993 | 0.9068 | 0.9158 | 0.9282 |
| | | | | | nloride Solutio | | | | |
| | | · · · · · · · · · · · · · · · · · · · | A | t Thermal Sa | aturation (C _{sa} | nt) | · · · · · · · · · · · · · · · · · · · | | ····· |
| 044 | 0.9721 | | 0.9791 | 0.9818 | | 0.9890 | 0.9993 | 1.0115 | |
| 996 | 0.9455 | | 0.9495 | 0.9542 | | 0.9609 | 0.9690 | 0.9806 | |
| 957 | 0.9202 | | 0.9235 | 0.9267 | | 0.9324 | 0.9403 | 0.9506 | |
| 877 | 0.8945 | | 0.8982 | 0.9013 | | 0.9064 | 0.9132 | 0.9216 | |
| | | | Å | At Constant I | Pressure (C _P |) | | | |
| .044 | 0.9722 | | 0.9793 | 0.9823 | | 0.9900 | 1.0011 | 1.0147 | |
| 996 | 0.9456 | | 0.9497 | 0.9547 | | 0.9618 | 0.9707 | 0.9836 | |
| .957 | 0.9203 | | 0.9237 | 0.9271 | | 0.9332 | 0.9419 | 0.9534 | |
| 877 | 0.8946 | | 0.8984 | 0.9017 | | 0.9072 | 0.9146 | 0.9241 | |
| | | | м | aonesium Si | ulfate Solutio | ns | | | |
| | | | | | aturation (C _{sa} | | | | |
| | | | | | | | | | or and or a |
| .101 | | 0.9835 | 0.9864 | | 0.9979 | 1.0037 | 1.0154 | 1.0309 | 1.0502 |
| .989 | 0.9609 | | 0.9675 | 0.9756 | | 0.9859 | 0.9988 | 1.0147 | |
| .029 | 0.9409 | | 0.9482 | 0.9571 | | 0.9675 | 0.9816 | 0.9982 | |
| .001 .994 | 0.9273 0.9050 | | 0.9307 0.9135 | 0.9401 0.9236 | | 0.9517 0.9348 | 0.9654 0.9497 | 0.9824 0.9676 | |
| | 0.5050 | | | | Dan an 10 | | 0.0407 | 0.0070 | |
| | <u> </u> | | | | Pressure (C _P |) | | | |
| .101 | | 0.9836 | 0.9866 | | 0.9986 | 1.0047 | 1.0172 | 1.0341 | 1.0556 |
| .989 | 0.9610 | | 0.9677 | 0.9761 | | 0.9868 | 1.0005 | 1.0177 | |
| 029 | 0.9410 | | 0.9484 | 0.9575 | | 0.9683 | 0.9832 | 1.0010 | |
| 001 | 0.9224 | | 0.9309 | 0.9405 | | 0.9525 | 0.9668 | 0.9849 | |
| .994 | 0.9051 | | 0.9137 | 0.9240 | | 0.9355 | 0.9510 | 0.9699 | |
| | | | | | ate Solutions | | | | |
| | | | | | | it/ | | | |
| | | | | | | | | | |
| .997 | 0.9822 | | 0.9861 | 0.9918 | | 0.9997 | 1.0101 | 1.0239 | |
| .954 | 0.9624 | | 0.9662 | 0.9721 | | 0.9789 | 0.9884 | 1.0007 | |
| .954 .957 | 0.9624 0.9442 | | 0.9662 0.9481 | 0.9721 0.9526 | | 0.9789 0.9598 | 0.9884 0.9678 | 1.0007 0.9798 | |
| .954 .957 .952 | 0.9624 0.9442 0.9271 | | 0.9662 0.9481 0.9317 | 0.9721 0.9526 0.9355 | | 0.9789 0.9598 0.9411 | 0.9884 0.9678 0.9492 | 1.0007 0.9798 0.9588 | |
| .954 .957 | 0.9624 0.9442 | | 0.9662 0.9481 0.9317 0.9146 | 0.9721 0.9526 0.9355 0.9182 | | 0.9789 0.9598 0.9411 0.9240 | 0.9884 0.9678 | 1.0007 0.9798 | |
| .954 .957 .952 | 0.9624 0.9442 0.9271 | | 0.9662 0.9481 0.9317 0.9146 | 0.9721 0.9526 0.9355 0.9182 | Pressure (C _P | 0.9789 0.9598 0.9411 0.9240 | 0.9884 0.9678 0.9492 | 1.0007 0.9798 0.9588 | |
| .954 .957 .952 .882 | 0.9624 0.9442 0.9271 0.9114 | | 0.9662 0.9481 0.9317 0.9146 | 0.9721 0.9526 0.9355 0.9182 At Constant | Pressure (C _P | 0.9789 0.9598 0.9411 0.9240 | 0.9884 0.9678 0.9492 0.9312 | 1.0007 0.9798 0.9588 0.9405 | |
| .954 .957 .952 | 0.9624 0.9442 0.9271 | | 0.9662 0.9481 0.9317 0.9146 | 0.9721 0.9526 0.9355 0.9182 | Pressure (C _P | 0.9789 0.9598 0.9411 0.9240 | 0.9884 0.9678 0.9492 | 1.0007 0.9798 0.9588 | |
| .954 .957 .952 .882 | 0.9624 0.9442 0.9271 0.9114 | | 0.9662 0.9481 0.9317 0.9146 0.9863 | 0.9721 0.9526 0.9355 0.9182 At Constant 0.9923 | Pressure (C _P | 0.9789 0.9598 0.9411 0.9240 | 0.9884 0.9678 0.9492 0.9312 1.0119 | 1.0007 0.9798 0.9588 0.9405 | |
| .954 .957 .952 .882 .997 .954 | 0.9624 0.9442 0.9271 0.9114 0.9823 0.9823 | | 0.9662 0.9481 0.9317 0.9146 0.9863 0.9863 | 0.9721 0.9526 0.9355 0.9182 At Constant 0.9923 0.9726 | Pressure (C _P | 0.9789 0.9598 0.9411 0.9240 | 0.9884 0.9678 0.9492 0.9312 1.0119 0.9901 | 1.0007 0.9798 0.9588 0.9405 1.0271 1.0037 | |

(Defined cal/g °C)

$$\overline{C_{P(w)}} = C_{P(w)}^{*} + \frac{\nu}{2} \frac{\sigma(1^{1/2})}{1000} \frac{A_{f}}{3} |Z_{+}Z_{-}|^{1/2}m +$$

$$\frac{\mathsf{B}}{1000} m^2 M_s + \dots \quad (4)$$

$$\overline{C_{P(s)}} = \overline{C_{P(s)}}^\circ + \frac{\nu}{2} |Z_+ Z_-| \frac{1^{1/2}}{1 + 1^{1/2}} \frac{A_j}{M_s} -$$

2Bm + ... (5)

Experimental Results

Measured values of the heat capacity at saturation, $C_{\rm sat}$, and the calculated values of the heat capacity at constant pressure C_p , from Equation 1 are given in Table I for various salts, salinities, and temperatures. The values should be accurate to ± 0.003 cal/g°C. Values of $C_{\rm sat}$ are also given in Figures 1 to 5.

Using these heat capacity values and extended Debye-Hückel theory as given above, it was possible to calculate the values for the heat capacity at infinite dilution, $\overline{C_{P(s)}}^{\circ}$, and the values of *B* (Table II).

Values of C_P at even salinities are given in Table III.

A limited number of apparent and partial quantities are presented in Table IV. The values at 0% salt are those for $\overline{C_P}(s)^{\circ}$ and pure water as given in Tables II and III, respectively.

Relative partial enthalpies of NaCl in aqueous solutions are given in Table V.

Conclusions

Experimental and calculated values for heat capacities of several salt solutions from 80 to 200° C are presented, as are the relative enthalpies for NaCl solutions. The latter results are in excellent agreement with other literature data [Likke (3), Smith and Hirtle (4), and White (5)].

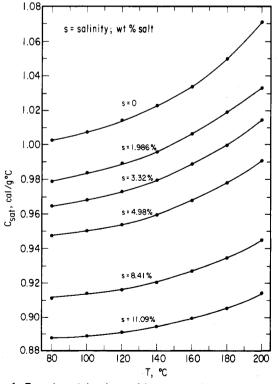


Figure 1. Experimental values of heat capacity at thermal saturation C_{sat} vs. 7 for NaCl

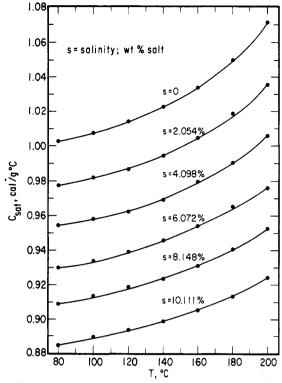


Figure 2. Experimental values of heat capacity at thermal saturation



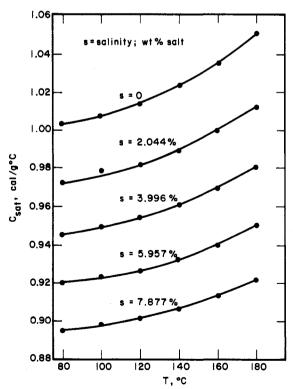


Figure 3. Experimental values of heat capacity at thermal saturation C_{6at} vs. 7 for MgCl₂

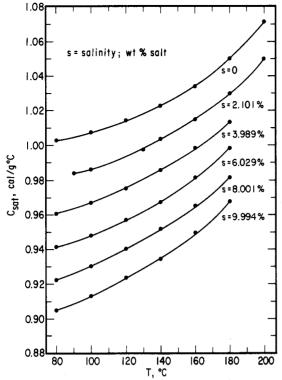
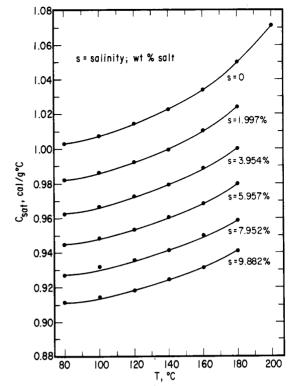


Figure 4. Experimental values of heat capacity at thermal saturation $C_{\rm sat}$ vs. 7 for MgSO4



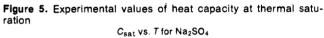


Table II. Values of $\overline{C}_{P(S)}^{\circ}$ and B in Extended Debye-Hückel Theory^a Determined from Experimental Data (Not smoothed with respect to temperature)

| * | NaCl | | K | KCI | | MgCi ₂ | | MgSO₄ | | Na₂SO₄ | |
|----------|-------------------------------|--------|-------------------------------|--------|-------------------------------|-------------------|-------------------------------|--------|-------------------------------|--------|--|
| °C ℃ | $\overline{C_{P(s)}}^{\circ}$ | В | $\overline{C_{P(s)}}^{\circ}$ | B | $\overline{C}_{P(s)}^{\circ}$ | В | $\overline{C_{P(s)}}^{\circ}$ | B | $\overline{C}_{P(s)}^{\circ}$ | В | |
| 80 | -0.0279 | -0.041 | -0.282 | -0.011 | -0.696 | -0.040 | -0.300 | +0.017 | -0.181 | -0.087 | |
| 100 | -0.308 | -0.030 | -0.316 | -0.021 | -0.654 | +0.098 | -0.275 | +0.069 | -0.222 | -0.087 | |
| 120 | -0.394 | -0.036 | -0.394 | -0.050 | -0.840 | +0.012 | -0.281 | +0.107 | -0.273 | -0.059 | |
| 140 | -0.505 | -0.047 | -0.450 | -0.042 | -0.976 | -0.001 | -0.298 | +0.170 | -0.360 | -0.060 | |
| 160 | -0.617 | -0.045 | -0.548 | -0.053 | -1.144 | +0.015 | -0.368 | +0.208 | -0.476 | -0.061 | |
| 180 | -0.785 | -0.047 | -0.647 | -0.033 | -1.372 | +0.038 | -0.472 | +0.278 | -0.604 | -0.005 | |
| 200 | -1.023 | -0.062 | -0.800 | -0.026 | | | | | | | |

| | moothed, 20- | -200 °C* |
|----------|--------------------------------|----------|
| °C °C | $\overline{C_P}_{(s)}^{\circ}$ | B |
| 20 | -0.385 | -0.111 |
| 40 | -0.318 | -0.090 |
| 60 | -0.255 | -0.045 |
| 80 | -0.270 | -0.038 |
| 100 | -0.292 | -0.020 |
| 120 | -0.397 | -0.038 |
| 140 | -0.504 | -0.047 |
| 160 | -0.619 | -0.046 |
| 180 | -0.786 | -0.047 |
| 200 | -1.024 | -0.062 |
| | | |

^a Units of $\overline{C_{P(s)}}^{\circ}$ are cal/g salt °C. Units of *B* are cal/g °C · kg water/g mol salt. ^b Data for 20–80 °C from Smith and Hirtle (4), Harned and Cook (2), and White (5). (Defined cal/g °C)

| | | | | | - | | | | | | | | - |
|-------------|--------|--------|--------|--------|--------|---------------------|------------|---------|--------|--------|--------|--------|--------|
| Temp, °C | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| | | | | | | NaCl, | wt % salt | | | | | | |
| 80 | 1.0030 | 0.9909 | 0.9794 | 0.9682 | 0.9573 | 0.9467 | 0.9363 | 0.9262 | 0.9163 | 0.9067 | 0.8973 | 0.8881 | 0.8792 |
| 100 | 1.0076 | 0.9953 | 0.9836 | 0.9723 | 0.9612 | 0.9503 | 0.9397 | 0.9293 | 0.9191 | 0.9091 | 0.8993 | 0.8897 | 0.8803 |
| 120 | 1.0145 | 1.0014 | 0.9891 | 0.9771 | 0.9655 | 0.9542 | 0.9432 | 0.9324 | 0.9219 | 0.9116 | 0.9015 | 0.8917 | 0.8822 |
| 140 | 1.0240 | 1.0100 | 0.9968 | 0.9842 | 0.9720 | 0.9602 | 0.9487 | 0.9375 | 0.9266 | 0.9161 | 0.9058 | 0.8959 | 0.8863 |
| 160 | 1.0368 | 1.0218 | 1.0079 | 0.9945 | 0.9816 | 0.9692 | 0.9570 | 0.9453 | 0.9338 | 0.9227 | 0.9119 | 0.9015 | 0.8913 |
| 180 | 1.0535 | 1.0371 | 1.0219 | 1.0075 | 0.9937 | 0.9803 | 0.9674 | 0.9548 | 0.9427 | 0.9309 | 0.9195 | 0.9084 | 0.8977 |
| 200 | 1.0747 | 1.0563 | 1.0396 | 1.0238 | 1.0088 | 0.9944 | 0.9806 | 0.9673 | 0.9546 | 0.9423 | 0.9305 | 0.9191 | 0.9082 |
| | | | | | | KCI, w | 't % salt | | | | | | |
| 80 | 1.0030 | 0.9906 | 0.9786 | 0.9668 | 0.9550 | 0.9434 | 0.9320 | 0.9206 | 0.9092 | 0.8980 | 0.8869 | 0.8758 | 0.8648 |
| 100 | 1.0076 | 0.9950 | 0.9828 | 0.9708 | 0.9590 | 0.9474 | 0.9359 | 0.9246 | 0.9134 | 0.9023 | 0.8914 | 0.8806 | 0.8699 |
| 120 | 1.0145 | 1.0012 | 0.9884 | 0.9760 | 0.9639 | 0.9521 | 0.9405 | 0.9292 | 0.9181 | 0.9073 | 0.8967 | 0.8863 | 0.8762 |
| 140 | 1.0240 | 1.0102 | 0.9970 | 0.9842 | 0.9717 | 0.9594 | 0.9474 | 0.9357 | 0.9242 | 0.9129 | 0.9018 | 0.8910 | 0.8804 |
| 160 | 1.0368 | 1.0221 | 1.0082 | 0.9947 | 0.9816 | 0.9689 | 0.9565 | 0.9444 | 0.9325 | 0.9210 | 0.9097 | 0.8987 | 0.8880 |
| 180 | 1.0535 | 1.0379 | 1.0232 | 1.0090 | 0.9952 | 0.9817 | 0.9686 | 0.9557 | 0.9431 | 0.9307 | 0.9185 | 0.9066 | 0.8949 |
| 200 | 1.0747 | 1.0577 | 1.0419 | 1.0267 | 1.0120 | 0.9977 | 0.9837 | 0.9700 | 0.9566 | 0.9434 | 0.9305 | 0.9178 | 0.9054 |
| | | | | | | MgCl ₂ , | wt % salt | | | | | | |
| 80 | 1.0030 | 0.9876 | 0.9731 | 0.9591 | 0.9455 | 0.9321 | 0.9190 | 0.9062 | 0.8935 | 0.8811 | 0.8689 | 0.8569 | 0.8450 |
| 100 | 1.0076 | 0.9928 | 0.9787 | 0.9649 | 0.9512 | 0.9374 | 0.9237 | 0.9098 | 0.8958 | 0.8817 | 0.8674 | 0.8530 | 0.8383 |
| 120 | 1.0145 | 0.9982 | 0.9831 | 0.9685 | 0.9543 | 0.9405 | 0.9268 | 0.9133 | 0.9000 | 0.8868 | 0.8738 | 0.8608 | 0.8480 |
| 140 | 1.0240 | 1.0068 | 0.9910 | 0.9758 | 0.9612 | 0.9469 | 0.9329 | 0.9191 | 0.9055 | 0.8922 | 0.8789 | 0.8659 | 0.8529 |
| 160 | 1.0368 | 1.0184 | 1.0018 | 0.9860 | 0.9707 | 0.9558 | 0.9413 | 0.9270 | 0.9129 | 0.8990 | 0.8852 | 0.8716 | 0.8581 |
| 180 | 1.0535 | 1.0336 | 1.0159 | 0.9992 | 0.9831 | 0.9676 | 0.9524 | 0.9374 | 0.9227 | 0.9082 | 0.8938 | 0.8795 | 0.8653 |
| | | | | | | MgSO₄ | , wt % sal | t | | | | | |
| 80 | 1.0030 | 0.9916 | 0.9811 | 0.9710 | 0.9611 | 0.9514 | 0.9418 | 0.9323 | 0.9229 | 0.9136 | 0.9044 | 0.8952 | 0.8860 |
| 100 | 1.0076 | 0.9967 | 0.9868 | 0.9773 | 0.9679 | 0.9587 | 0.9495 | 0.9404 | 0.9313 | 0.9221 | 0.9129 | 0.9037 | 0.8944 |
| 120 | 1.0145 | 1.0039 | 0.9943 | 0.9852 | 0.9763 | 0.9675 | 0.9587 | 0.9499 | 9.9410 | 0.9321 | 0.9231 | 0.9139 | 0.9047 |
| 140 | 1.0240 | 1.0136 | 1.0044 | 0.9957 | 0.9871 | 0.9786 | 0.9701 | 0.9614 | 0.9527 | 0.9437 | 0.9345 | 0.9251 | 0.9155 |
| 160 | 1.0368 | 1.0263 | 1.0173 | 1.0088 | 1.0006 | 0.9925 | 0.9843 | 0.9760 | 0.9675 | 0.9589 | 0.9500 | 0.9408 | 0.9313 |
| 180 | 1.0535 | 1.0203 | 1.0339 | 1.0258 | 1.0179 | 1.0101 | 1.0023 | 0.9942 | 0.9860 | 0.9389 | 0.9500 | 0.9408 | 0.9313 |
| 100 | 1.0555 | 1.0427 | 1.0555 | 1.0250 | 1.0179 | 1.0101 | 1.0025 | 0.9942 | 0.9800 | 0.9774 | 0.9085 | 0.9592 | 0.9490 |
| | | | | | | Na ₂ SO | , wt % sal | lt | | | | | |
| 80 | 1.0030 | 0.9921 | 0.9819 | 0.9720 | 0.9626 | 0.9532 | 0.9441 | 0.9354 | 0.9268 | 0.9185 | 0.9104 | 0.9025 | 0.8948 |
| 100 | 1.0076 | 0.9965 | 0.9861 | 0.9761 | 0.9664 | 0.9571 | 0.9480 | 0.9392 | 0.9307 | 0.9224 | 0.9143 | 0.9065 | 0.8989 |
| 120 | 1.0145 | 1.0029 | 0.9922 | 0.9820 | 0.9721 | 0.9624 | 0.9531 | 0.9439 | 0.9350 | 0.9263 | 0.9178 | 0.9095 | 0.9013 |
| 140 | 1.0240 | 1.0118 | 1.0006 | 0.9899 | 0.9796 | 0.9696 | 0.9600 | 0.9506 | 0.9414 | 0.9325 | 0.9238 | 0.9153 | 0.9070 |
| 160 | 1.0368 | 1.0237 | 1.0118 | 1.0006 | 0.9898 | 0.9794 | 0.9693 | *0.9596 | 0.9501 | 0.9409 | 0.9320 | 0.9233 | 0.9148 |
| 180 | 1.0535 | 1.0394 | 1.0268 | 1.0149 | 1.0036 | 0.9925 | 0.9818 | 0.9714 | 0.9612 | 0.9512 | 0.9414 | 0.9318 | 0.9223 |
| | | | | | | | | | | | | | |

Table IV. Apparent and Partial (Unit Mass) Heat Capacity Values for Salts and Water (Defined cal/g $^{\circ}C)$

| _ | - | 4% | | | 8% | | 12% | | |
|-----|-------------------|-----------------------|-----------------------|-------------------|-----------------------|-----------------------|-------------------|-----------------------|-----------------------|
| °C | $(\phi C_{P(s)})$ | $\overline{C_{P(s)}}$ | $\overline{C}_{P(w)}$ | $(\phi C_{P(s)})$ | $\overline{C_{P(s)}}$ | $\overline{C_{P}(w)}$ | $(\phi C_{P(s)})$ | $\overline{C_{P(s)}}$ | $\overline{C}_{P(w)}$ |
| 80 | -0.139 | -0.075 | 1.0015 | -0.080 | +0.108 | 0.9998 | -0.028 | +0.106 | 0.9978 |
| 100 | -0.154 | -0.091 | 1.0059 | -0.099 | -0.010 | 1.0037 | -0.053 | +0.061 | 1.0014 |
| 120 | -0.209 | -0.133 | 1.0124 | -0.143 | -0.036 | 1.0098 | -0.088 | +0.050 | 1.0071 |
| 140 | -0.277 | -0.182 | 1.0215 | -0.193 | -0.058 | 1.0184 | -0.124 | +0.053 | 1.0150 |
| 160 | -0.343 | -0.236 | 1.0337 | -0.251 | -0.103 | 1.0298 | -0.176 | +0.011 | 1.0256 |
| 180 | -0.442 | -0.312 | 1.0495 | -0.332 | -0.158 | 1.0444 | -0.245 | -0.030 | 1.0391 |
| 200 | -0.572 | -0.401 | 1.0694 | -0.427 | -0.198 | 1.0628 | -0.312 | -0.029 | 1.0558 |

(Continued on page 194)

| Tama | | 4% | | | 8% | | 12% | | | |
|------|-------------------|-----------------------|---------------------|---------------------|-------------|---------------------|-------------------|---------------------|---------------------|--|
| °C | $(\phi C_{P(s)})$ | $\overline{C_{P}}(s)$ | $\overline{C_P}(w)$ | $(\phi C_{P(s)})$ | CP(s) | $\overline{C_P}(w)$ | $(\phi C_{P(s)})$ | $\overline{C_P}(s)$ | $\overline{C_P}(w)$ | |
| | | | | KCI, v | wt % salt | | | | | |
| 80 | -0.196 | -0.163 | 1.0019 | -0.169 | -0.127 | 1.0005 | -0.148 | -0.099 | 0.9990 | |
| 100 | -0.208 | -0.164 | 1.0063 | -0.170 | -0.111 | 1.0046 | -0.140 | -0.066 | 1.0028 | |
| 120 | -0.250 | -0.184 | 1.0129 | -0.190 | -0.090 | 1.0109 | -0.138 | -0.003 | 1.0083 | |
| 140 | -0.285 | -0.216 | 1.0221 | -0.224 | -0.125 | 1.0197 | -0.173 | -0.044 | 1.0170 | |
| 160 | -0.343 | -0.257 | 1.0344 | -0.267 | -0.143 | 1.0314 | -0.204 | -0.043 | 1.028 | |
| 180 | -0.404 | -0.312 | 1.0504 | -0.327 | -0.208 | 1.0465 | -0.268 | -0.125 | 1.0423 | |
| 200 | -0.492 | -0.381 | 1.0707 | -0.401 | -0.266 | 1.0655 | -0.336 | -0.181 | 1.0599 | |
| | | | | MgCl ₂ , | wt % salt | | | | | |
| 80 | -0.435 | -0.349 | 1.0002 | -0.365 | -0.259 | 0.9970 | | | | |
| 100 | -0.404 | -0.365 | 1.0042 | -0.390 | -0.396 | 1.0004 | | | | |
| 120 | -0.489 | -0.392 | 1.0104 | -0.417 | -0.318 | 1.0058 | | | | |
| 140 | -0.547 | -0.427 | 1.0191 | -0.457 | -0.334 | 1.0134 | | | | |
| 160 | -0.617 | -0.475 | 1.0306 | -0.513 | -0.375 | 1.0236 | | | | |
| 180 | -0.705 | -0.532 | 1.0456 | -0.582 | -0.422 | 1.0366 | | | | |
| | | | | MgSO₄ | , wt % salt | | | | | |
| 80 | -0.045 | 0.021 | 1.0000 | 0.002 | 0.063 | 0.9966 | 0.028 | 0.081 | 0.9932 | |
| 100 | 0.015 | 0.077 | 1.0040 | 0.053 | 0.091 | 1.0000 | 0.064 | 0.072 | 0.9959 | |
| 120 | 0.059 | 0.126 | 1.0102 | 0.096 | 0.124 | 1.0053 | 0.099 | 0.081 | 1.0004 | |
| 140 | 0.102 | 0.169 | 1.0188 | 0.132 | 0.137 | 1.0129 | 0.119 | 0.052 | 1.0068 | |
| 160 | 0.131 | 0.217 | 1.0303 | 0.171 | 0.181 | 1.0229 | 0.157 | 0.079 | 1.0154 | |
| 180 | 0.164 | 0.269 | 1.0451 | 0.209 | 0.213 | 1.0357 | 0.187 | 0.073 | 1.0261 | |
| | | | | Na₂SO₄ | , wt % salt | | | | | |
| 80 | -0.010 | 0.059 | 1.0011 | 0.051 | 0.150 | 0.9990 | 0.102 | 0.231 | 0.9966 | |
| 100 | -0.022 | 0.056 | 1.0054 | 0.046 | 0.155 | 1.0028 | 0.101 | 0.241 | 1.0000 | |
| 120 | -0.046 | 0.035 | 1.0118 | 0.021 | 0.124 | 1.0087 | 0.072 | 0.195 | 1.0053 | |
| 140 | -0.086 | 0.008 | 1.0208 | -0.009 | 0.109 | 1.0170 | 0.049 | 0.188 | 1.0129 | |
| 160 | -0.139 | -0.025 | 1.0328 | -0.047 | 0.092 | 1.0280 | 0.020 | 0.181 | 1.0230 | |
| 180 | -0.195 | -0.071 | 1.0484 | -0.100 | 0.033 | 1.0422 | -0.040 | 0.095 | 1.0357 | |

(Defined cal/g $^{\circ}$ C)

Table V. Relative Partial Enthalpies of NaCl in Aqueous Solutions

| | (Defined cal/g) | | | | | | | | | | | | |
|-----|-----------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--------|--|--|
| | | wt % | | | | | | | | | | | |
| °C | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | | |
| 25 | 0 | 1.55 | 0.71 | -0.36 | 1.52 | -2.66 | -3.75 | -4.80 | -5.79 | -6.72 | - 7.58 | | |
| 50 | 0 | 3.66 | 3.92 | 3.80 | 3.57 | 3.36 | 3.17 | 3.03 | 2.95 | 2.94 | 3.02 | | |
| 75 | 0 | 6.04 | 7.25 | 7.90 | 8.37 | 8.81 | 9.26 | 9.74 | 10.27 | 10.87 | 11.5 | | |
| 100 | 0 | 8.83 | 11.00 | 12.39 | 13.49 | 14.49 | 15.47 | 16.46 | 17.49 | 18.57 | 19.73 | | |
| 150 | 0 | 16.58 | 21.26 | 24.48 | 27.11 | 29.48 | 31.71 | 33.88 | 36.04 | 38.22 | 40.45 | | |
| 200 | 0 | 30.01 | 38.92 | 45.19 | 50.35 | 54.93 | 59.19 | 63.25 | 67.22 | 71.14 | 75.07 | | |

Nomenclature

 A_i = Debye-Hückel constant [see Bromley et al. (1), Table III for values

B = constant (see Table II and Equations 3 to 5)

 C_P = heat capacity of solution at constant pressure, cal/g°C

 C_{sat} = heat capacity of solution at saturation, cal/g°C

 $(\phi C_{P(s)})$ = apparent heat capacity of salts, cal/g salts°C $\overline{C}_{P(s)}$ = partial heat capacity of salts in solution, cal/g salts°C

- $\overline{C}_{P(s)}^{\circ}$ = partial heat capacity of salts at infinite dilution, cal/g salts°C
- $C_{P(w)}^*$ = heat capacity of pure water at constant pressure, cal/g°C

 $\overline{C_{P(w)}}$ = partial heat capacity of water in solution, cal/g water °C

 $I = \text{ionic strength} = \sum m_i Z_i^{2/2}$

 M_i = molecular weight of ion i

 M_s = molecular weight of salt

m = molality = gram moles salt/1000 grams water

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P = \text{pressure}
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- S = salinity in weight per cent salt
- T = temperature, K
- u = specific volume of saturated liquid, cm³/g
- x = mass fraction of liquid in calorimeter
- Z_i = charge on ion *i*
- ν = number of ions per molecule of salt
- σ = standard deviation

$$\sigma(l^{1/2})/3 = (1/l^{3/2}) \begin{bmatrix} 1 + l^{1/2} - 1/(1 + l^{1/2}) - 2 \ln \\ (1 + l^{1/2}) \end{bmatrix}$$

Literature Cited

- Bromley, L. A., Diamond, A. E., Salami, E., Wilkins, D. G., J. Chem. Eng. Data, 15, 246 (1970).
 Harned, H. S., Cook, M. A., J. Amer. Chem. Soc., 61, 495 (1939).
- Likke, S., Ph.D. thesis, University of California, Berkeley, Calif., (3)
- 1972
- (4) Smith, R. P., Hirtle, D. S., J. Amer. Chem. Soc., 61, 1126 (1939).
- (5) White, C. M., J. Phys. Chem., 44, 494 (1940).

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Measured Enthalpies of Eight Hydrocarbon Fractions

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Measured enthalpy values are reported for five naphthas, a kerosine, a fuel oil, and a gas oil in the temperature range 155 to 640°F for pressures up to 1400 psia.

Because of the relatively unsatisfactory ability to predict accurately enthalpy values for hydrocarbon fractions, the American Petroleum Institute authorized the measurement of a series of hydrocarbon fractions with the intent of providing data for checking the accuracy of existing prediction procedures and for use in the potential development of new improved enthalpy prediction methods. The materials measured comprised a very close-boiling naphtha from the north slope of Alaska, a jet fuel naphtha, a very aromatic naphtha from a cracking furnace, two straight-run paraffinic Pennsylvania naphthas, a California kerosine, a grade number 2 fuel oil, and a gas oil.

Previously, the results for a California naphtha were reported (3). The properties of the materials measured were determined in detail, and are listed in Tables I and II. These properties include density, Watson factor, molecular weight, critical temperature and pressure, heat of combustion, refractive dispersion, ASTM and TBP distillations, and compositions.

Experimental

The mole percent of the various kinds of hydrocarbons in each material was established by use of mass spectrograph analysis. The analyses, the molecular weight, and the refractive dispersion were determined at the Union Oil Co. laboratories. The critical properties of the Alaska naphtha were measured by W. B. Kay at the Ohio State University. The critical constants for the jet naphtha and the low-boiling naphtha were established from the enthalpy measurements. The other critical properties tabulated represent estimates obtained by using the procedures in the API data book (1).

The enthalpy measurements were made with a flow calorimeter, one in operation since 1967. This calorimeter measures the difference in enthalpy between the fluid entering the calorimeter at a relatively high temperature and a departing temperature of 75°F, at the pressure of measurement. The calorimeter operates isobarically. Repeatedly this apparatus has been shown to have an accuracy level of 1.5 Btu/lb, determined by measurements of the enthalpy of pure n-pentane, and liquid water, with comparison to literature values presented for these two pure components (2, 5). The calorimeter has been previously described (4).

Results and Discussion

This study represents 1013 measurements. The actual measured data have been tabulated relative to the liquid state at 75°F and the pressure of measurement, and have been deposited with the ACS Microfilm Depository Service. The measured data were converted to a base level of 75°F and the saturated liquid condition with the use of the thermodynamic equation of state as previously discussed (4). Since this correction for the change of enthalpy with pressure is computed for the liquid phase at a temperature greatly lower than the critical temperature, the conversion can be computed with a precision in excess of the accuracy of the calorimeter measurements. Following this correction for pressure level, smoothed values were obtained by cross-plotting on large scale graph paper. These smoothed results are presented in Tables III-X.

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