

# National Bureau of Standards

## Certificate

### Standard Reference Material 1655

#### Potassium Chloride, KCl(cr) for Solution Calorimetry

This Standard Reference Material is intended for use in verifying or comparing results obtained by calorimeters measuring enthalpies of endothermic solution processes. Normally, electrical energy calibrations are performed, and deviation of measured values from the certified value for the enthalpy of solution may serve as an indication of systematic errors in the calorimetry. If proper measuring instruments for electrical energy calibration are not available, the material may be used as a standard for calibrating a calorimeter.

This material is certified with respect to the enthalpy of the endothermic process of solution in water when carried out under the specified conditions that are described on the following pages.

The energy absorbed during the solution of SRM 1655 in distilled water at 298.15 K to form a solution with molality  $m = 0.111 \text{ mol} \cdot \text{kg}^{-1}$  is

$$(235.86 \pm 0.23) \text{ J} \cdot \text{g}^{-1}[1].$$

Before measurement, this material should be dried for at least 4 hours at 800 K. The uncertainty (0.10 percent) is the square root of the sum of the squares of the experimental imprecision at the 95 percent confidence level, 0.097 percent; the uncertainty in the thermal coefficient and the thermodynamic temperature of the reaction, 0.011 percent; and the uncertainty in the mass and moisture content of the material, 0.006 percent.

The above value is based on a comparison of the reaction energy with electrical energy measured in terms of the national standards of resistance, electromotive force, and time. The platinum-lined silver, vacuum-jacketed, adiabatic solution calorimeter, electrical measuring instruments, procedures used for the measurements, and corrections to the experimental data have been described [2, 3, and 4].

The overall direction and coordination leading to the certification of the enthalpy change were performed by G.T. Armstrong and D. Garvin. The technical measurements were made by M.V. Kilday in the Chemical Thermodynamics Division.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by R.K. Kirby.

Washington, D.C. 20234  
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George A. Uriano, Chief  
Office of Standard Reference Materials

The material used for this SRM is a portion of SRM 999, an analytical standard of known potassium and chloride content. The assay after drying was 99.98 mass percent based on the potassium determination and 99.99 mass percent based on the chloride determination. The material as received contains approximately 0.1 mass percent occluded water. For details of the chemical composition and analyses, see [5]. The molar masses used in this chemical analysis were  $39.098 \text{ g} \cdot \text{mol}^{-1}$  for potassium and  $35.453 \text{ g} \cdot \text{mol}^{-1}$  for chlorine.

#### Procedures and Corrections:

This standard reference material should be used without further crushing. It should be heated for at least 4 hours at  $(800 \pm 10) \text{ K}$  to remove occluded water and then cooled in a desiccator. (Caution: Crucibles for heating the material must have melting temperatures well above  $800 \text{ K}$  and be inert and non-contaminating to KCl.)

This material is not hygroscopic below 75 percent relative humidity (RH) at  $\approx 295 \text{ K}$  and may be weighed in air; the weighings should be corrected to vacuum using the density,  $1.98 \text{ g} \cdot \text{cm}^{-3}$ , for KCl. The buoyancy factor, 1.000455, may be used for normal laboratory conditions  $[(35 \pm 15)\% \text{ RH}, (295 \pm 1) \text{ K}, (0.10 \pm 0.01) \text{ MPa}$  or  $(750 \pm 10) \text{ Torr}$ , and air density  $= (1180 \pm 25) \mu\text{g} \cdot \text{cm}^{-3}]$ . The molar mass of KCl is taken as  $74.5513 \text{ g} \cdot \text{mol}^{-1}$ [6].

Calorimetric procedures for dissolution processes have been discussed by many authors. Some of the more recent pertinent treatments are discussed [2, 4, 7-11]. Only a few recommended general procedures are mentioned here for emphasis.

Standard endothermic reactions should be used for the confirmation of measurement accuracy or for the calibrations of unknown endothermic reactions using the same calorimeter and procedures; and standard exothermic reactions, for unknown exothermic reactions.

Visual confirmation of adequate stirring for each reaction studied should be made. This is especially important if there is a large difference between the densities of the solute and the solvent as there is for KCl and  $\text{H}_2\text{O}$ .

For highest accuracy, calibrations of both the initial and final systems should be made for each reaction measured.

The sign, magnitude, and time for the temperature changes should be, as nearly as possible, the same for the calibrations and for the unknown reaction. If this cannot be accomplished, the magnitude of the resulting errors should be determined (see [8]).

Errors may result from condensation of moisture in measurements using a calorimeter with a constant temperature environment. To prevent these, the temperature of the environment should be maintained above the highest temperature of the reaction vessel, unless the reaction vessel is hermetically sealed.

General sources of error in solution calorimetry have been discussed [2, 3, 7, 12]. Also given elsewhere are possible sources of error in electrical energy measurements [2, 9] and in various features in calorimeter design [2, 8, 10].

In order to obtain the certified value for the enthalpy of solution of SRM 1655, certain corrections must be made to the measured enthalpy values unless the measurements are made at the temperature and molality to which the certified value refers. Departures from these conditions in the measurements should be small in order to minimize uncertainties in the corrections.

The temperature of the solution process should be within  $\pm 3 \text{ K}$  of the reference temperature,  $298.15 \text{ K}$ . Over this range, the measured temperature coefficient for the enthalpy of solution at the molality,  $m = 0.111 \text{ mol} \cdot \text{kg}^{-1}$ , is

$$\Delta C_p = -(2.076 \pm 0.087) \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1} \text{ or } -(154.8 \pm 6.4) \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} [4].$$

The enthalpy of solution at the reference temperature,

$$\Delta H^\circ(298.15 \text{ K}) = \Delta H(T_m) - (T_m - 298.15 \text{ K})\Delta C_p,$$

where  $T_m$  is the mean temperature of the solution process, and  $\Delta H(T_m)$  is the measured enthalpy of solution at that temperature. At other molalities,  $\Delta C_p$  can be calculated from the heat capacity of KCl(cr) at the reference temperature,  $C_p^\circ = 51.30 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  [13], and the apparent molal heat capacity of the final solution,  $\Phi_c$ .  $\Phi_c$  can be obtained from the equation of Singh, Woolley, McCurdy, and Hepler [14]:

$$\Phi_c = \Phi_c^\circ + 28.95 m^{1/2} + B m$$

where  $m$  is the molality,  $\Phi_c^\circ$  for KCl is  $-(114.1 \pm 0.2) \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ , and  $B$  for KCl is  $(6.7 \pm 0.7)$ . Then  $\Delta C_p = \Phi_c - C_p^\circ$ .

The enthalpy-of-solution measurements should be made at the molality of the certified enthalpy value,  $0.111 \text{ mol} \cdot \text{kg}^{-1}$ . If this condition is impossible, the measured enthalpy of solution of SRM 1655 should be corrected to  $m = 0.111 \text{ mol} \cdot \text{kg}^{-1}$  or  $n = 500$  for the system,  $\text{KCl} + n\text{H}_2\text{O}$ .

$$\Delta H^\circ(500 \text{ H}_2\text{O}, 298.15 \text{ K}) = \Delta H(n\text{H}_2\text{O}, 298.15 \text{ K}) - \{\Phi_L(n\text{H}_2\text{O}) - \Phi_L(500 \text{ H}_2\text{O})\}$$

where  $\Delta H(n\text{H}_2\text{O}, 298.15 \text{ K})$  is the measured enthalpy of solution corrected to the reference temperature, and the last term corrects it to the molality of the certified value. Some values for  $\{\Phi_L(n\text{H}_2\text{O}) - \Phi_L(500 \text{ H}_2\text{O})\}$  derived from Parker's tabulation [15] are given in footnote [16]. It is estimated that the uncertainty in the correction does not exceed  $5 \text{ J} \cdot \text{mol}^{-1}$  for the highest concentration given.

Some corrections to the measured energy of solution,  $Q$ , are usually small or negligible, but must be considered for both constant pressure and constant volume solution calorimeters;  $q_{\text{cond}}$  is the correction for the energy of condensation of water from the vapor space above the solution during the experiment, and  $q_{\text{vap}}$  is the correction for the energy of vaporization of water in saturating the air space in the sample container after it is opened.

$$-\Delta H(n\text{H}_2\text{O}, T_m) = Q - q_{\text{cond}} - q_{\text{vap}}$$

where  $Q$  is the product of the corrected temperature change and the energy equivalent of the system. The value certified here was derived from measurements in a constant pressure calorimeter; the vapor space was  $\approx 30 \text{ cm}^3$ ,  $q_{\text{cond}} \approx -0.006 \text{ J}$ , and  $q_{\text{vap}} \approx 0.06 \text{ J}$ .

The correction,  $q_{\text{cond}}$ , is necessary when there is a difference in the vapor pressures of water over the initial and final solutions. For measurements at constant pressure,

$$q_{\text{cond}} = (-\Delta H_{\text{vap}}) \left( \frac{p_w - p_s}{p_w} \right) V_v c.$$

$p_w$  is the vapor pressure of water at the temperature of the solution process,  $p_s$  is the vapor pressure of water over the final solution at  $T_m$ ,  $V_v$  is the volume of the vapor space above the solution,  $c$  is the mass concentration of SRM 1655, and  $\Delta H_{\text{vap}}$  is the enthalpy of vaporization of water per unit volume of saturated vapor at  $T_m$ . In constant volume measurements,  $\Delta E_{\text{vap}}$  is used instead of  $\Delta H_{\text{vap}}$  (see footnote [18]).  $p_s = a_m \cdot p_w$  where  $a_m$  is the activity of water in the final solution; and  $\ln a_m = -\Phi_m \nu m M \times 10^{-3}$  in which  $\Phi_m$  is the molal osmotic coefficient for the KCl solution [19],  $\nu$  is the number of ions per molecule dissociated for the 1:1 electrolyte ( $\nu = 2$  for KCl),  $m$  is the molality of the final solution, and  $M$  is the molar mass of water,  $18.0152 \text{ g} \cdot \text{mol}^{-1}$  [6]. In footnote [20] are listed values for  $\Phi_m$ ,  $a_m$ , and  $p_s$  based on the  $\Phi_m$  values of Hamer and Wu [19] and calculated for a range of molalities. These can be used in the calculation of  $q_{\text{cond}}$ .

The correction,  $q_{\text{vap}}$ , is for the vaporization of  $\text{H}_2\text{O}$  in saturating the space in the sample container. At constant pressure,

$$q_{\text{vap}} = (1 - \text{RH})\Delta H_{\text{vap}}V_s.$$

$\Delta H_{\text{vap}}$  is defined above. RH is the relative humidity of the atmosphere in which the sample container was filled.  $V_s$  is the space in the sample container not occupied by the sample, and

$$V_s = V_c - (m_s/d_s)$$

where  $V_c$  is the internal volume of the sample container,  $m_s$  is the mass of KCl, and  $d_s$  is the density of KCl,  $1.98 \text{ g} \cdot \text{cm}^{-3}$ .

The certified value for the enthalpy of solution of SRM 1655,  $\Delta H^\circ(500 \text{ H}_2\text{O}, 298.15 \text{ K}) = (17.584 \pm 0.017) \text{ kJ} \cdot \text{mol}^{-1}$ , is in good agreement with comparable values from the evaluations of measurements on other KCl samples of high purity:  $(17.55 \pm 0.04) \text{ kJ} \cdot \text{mol}^{-1}$  recommended by the Physical Chemistry Division of IUPAC in 1974 [21], and  $(17.56 \pm 0.04) \text{ kJ} \cdot \text{mol}^{-1}$ , Parker's "best" value selected from measurements reported prior to 1963 [15] corrected to  $n = 500$ .

When the correction,  $0.343 \text{ kJ} \cdot \text{mol}^{-1}$  [15], is subtracted from the certified value, the enthalpy of solution at infinite dilution is obtained:

$$\Delta H^\circ(\infty \text{H}_2\text{O}, 298.15 \text{ K}) = (17.241 \pm 0.018) \text{ kJ} \cdot \text{mol}^{-1}$$

## Footnotes and References

- [1] The joule (J) is one newton-meter and the gram (g) is  $10^{-3}$  kilogram as defined in the International System of Units (SI).
- [2] Prosen, E.J., and Kilday, M.V., An Adiabatic Solution Calorimeter and Measurements of a Standard Reaction for Solution Calorimetry, J. Res. Nat. Bur. Stand. (U.S.), **77A**, (Phys. and Chem.), No. 2, 179-203 (Mar.-Apr. 1973).
- [3] Prosen, E.J., and Kilday, M.V., Enthalpies of Reaction of Tris(hydroxymethyl)aminomethane in HCl (aq) and in NaOH (aq), J. Res. Nat. Bur. Stand. (U.S.), **77A**, (Phys. and Chem.), No. 5, 581-597 (Sept.-Oct. 1973).
- [4] Kilday, M.V., The Enthalpy of Solution of SRM 1655 (KCl) in H<sub>2</sub>O, J. Res. Nat. Bur. Stand. (U.S.), **85**, No. 6, 467-481 (Nov.-Dec. 1980).
- [5] National Bureau of Standards (U.S.) Certificate of Analysis, Standard Reference Material 999, Potassium Chloride, Office of Standard Reference Materials, Washington, D.C. 20234 (September 6, 1972).
- [6] Commission on Atomic Weights, Pure and Appl. Chem., **47**, 75-95 (1976).
- [7] Coughlin, J.P., Experimental Thermochemistry, Vol. 2, Chapter 14, edited by H.A. Skinner, Interscience Publishers, New York (1962).
- [8] Kilday, M.V., Systematic Errors in an Isoperibol Solution Calorimeter Measured with Standard Reference Reactions, J. Res. Nat. Bur. Stand. (U.S.), **85**, 449-465 (Nov.-Dec. 1980).
- [9] Brunetti, A.P., Prosen, E.J., and Goldberg, R.N., The Enthalpy of Reaction of Tris(hydroxymethyl)aminomethane with Hydrochloric Acid, J. Res. Nat. Bur. Stand. (U.S.), **77A**, (Phys. and Chem.), No. 5, 599-606 (Sept.-Oct. 1973).
- [10] Sunner, S., and Wadsö, I., A Precision Calorimetric System, Science Tools **13**, 1-6 (1966).
- [11] Montgomery, R.L., Melaugh, R.A., Lau, C.-C., Meier, G.H., Chan, H.H., and Rossini, F.D., Determination of the Energy Equivalent of a Water Solution Calorimeter with a Standard Substance, J. Chem. Thermodynamics **9**, 915-936 (1977).
- [12] Efimov, M.E., Klevaichuk, G.N., Medvedev, V.A., and Kilday, M.V., Enthalpies of Solution of KBr, KI, KIO<sub>3</sub>, and KIO<sub>4</sub> in H<sub>2</sub>O, J. Res. Nat. Bur. Stand. (U.S.), **84**, No. 4, 273-286 (July-Aug. 1979).
- [13] Wagman, D.D., Evans, W.H., Parker, V.B., Schumm, R.H., and Nuttall, R.L., Selected Values of Chemical Thermodynamic Properties, Nat. Bur. Stand. (U.S.) Tech. Note 270-8, in press.
- [14] Singh, P.P., Woolley, E.M., McCurdy, K.G., and Hepler, L.G., Heat Capacities of Aqueous Electrolytes: Eight 1:1 Electrolytes and  $\Delta C_p^\circ$  for Ionization of Water at 298 K, Can. J. Chem. **54**, 3315-3318 (1976).
- [15] Parker, V.B., Thermal Properties of Uni-univalent Electrolytes, Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.) **2**, 66 pages (Apr. 1965).

[16] The following values were obtained from [15]:

$n$	$m$	$\Phi_L, (n\text{H}_2\text{O})$	$\Phi_L(n\text{H}_2\text{O}) - \Phi_L(500 \text{ H}_2\text{O})$
	$\text{mol} \cdot \text{kg}^{-1}$	$\text{J} \cdot \text{mol}^{-1}$	$\text{J} \cdot \text{mol}^{-1}$
1000	0.05551	293	-50
900	.0617	301	-42
800	.0694	310	-33
700	.0793	322	-21
600	.0925	330	-13
500	.1110	343	0
400	.1388	351	8
300	.1850	356	13
200	.2775	339	-4
100	.5551	209	-134

[17] Properties of Water and Steam in SI-Units, prepared by Ernst Schmidt, Springer-Verlag New York, Inc. (1969).

[18] The following values obtained from [17] may be used in calculating  $q_{\text{cond}}$  and  $q_{\text{vap}}$ :

$T$	$\Delta H_{\text{vap}}$	$\Delta E_{\text{vap}}$	$p_w$
K	$\text{J} \cdot \text{cm}^{-3}$	$\text{J} \cdot \text{cm}^{-3}$	kPa
293	0.0424	0.0401	2.337
298	.0563	.0531	3.166
303	.0738	.0696	4.241

[19] Hamer, W.J., and Wu, Y.-C., Osmotic Coefficients and Mean Activity Coefficients of Uni-univalent Electrolytes in Water at 25 °C, J. Phys. Chem. Ref. Data, 1, No. 4, 1047-1100 (1972).

[20] The following values for KCl at 298.15 K obtained from [19] may be used in the calculation of  $q_{\text{cond}}$ :

$m$	$\Phi_m$	$a_m$	$p_s$	$(p_w - p_s)/p_w$
$\text{mol} \cdot \text{kg}^{-1}$			kPa	
0.05	0.940	0.998	3.161	0.002
.10	.927	.997	3.155	.003
.20	.913	.993	3.145	.007
.30	.906	.990	3.135	.010
.40	.902	.987	3.125	.013

The ratio given in the last column is valid in the interval about  $\pm 3$  K of the reference temperature.

[21] Cox, J.D., Collator, Section: Enthalpy, in Recommended Reference Materials for Realization of Physicochemical Properties, E.F.G. Herington, Editor, Pure and Appl. Chem. 40, 432-433 (1974).