

The vapour pressures of saturated aqueous solutions of potassium bromide, ammonium sulfate, copper(II) sulfate, iron(II) sulfate, and manganese(II) dichloride, at temperatures from 283 K to 308 K

Alexander Apelblat

Department of Chemical Engineering, Ben Gurion University of the Negev, Beer Sheva, Israel

(Received 22 June 1993)

Vapour pressures of saturated aqueous solutions of KBr, $(\text{NH}_4)_2\text{SO}_4$, CuSO_4 , FeSO_4 , and MnCl_2 were measured in the 283 K to 308 K temperature range using an evaporimetric technique and were compared with the literature values. From the vapour pressures, the water activities, osmotic coefficients, and molar enthalpies of vaporization and solution at saturation were evaluated.

1. Introduction

The use of saturated solutions to control atmospheric humidity and by this to maintain solid materials with desired water content is a traditional and most convenient practice in laboratory and industry.^(1–2) Vapour pressures over saturated solutions are known in the literature^(1–6) for most of the common inorganic salts, but the available values are not always accurate (especially if they are from very early sources) or complete enough with regard to the range of temperature.

Recently, systematic measurements of vapour pressures over saturated solutions of 10 inorganic salts were performed,^(7,8) applying the evaporimetric technique.⁽⁹⁾ In this work vapour pressures, water activities, and osmotic coefficients, as a function of temperature are presented for KBr, $(\text{NH}_4)_2\text{SO}_4$, CuSO_4 , FeSO_4 , and MnCl_2 . The temperature dependences of vapour pressures at saturation permit evaluation of enthalpy changes associated with the simultaneously occurring evaporation and crystallization processes.^(10–13) Reported vapour pressures are compared with the corresponding isoteniscopic and isopiestic measurements.^(3,6,15)

2. Experimental

Analar grade KBr, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ were supplied by Merck, $(\text{NH}_4)_2\text{SO}_4$ by Reidel de Haen, and CuSO_4 by Frutarom Laboratory Chemicals Ltd,

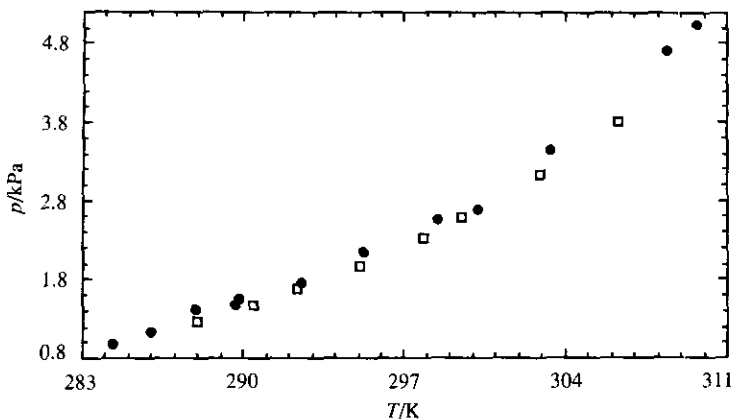


FIGURE 1. Vapour pressure of saturated KBr(aq) as a function of temperature. □, Reference 4; ●, this work.

Haifa. All reagents were used in experiments without further purification. Vapour pressures were determined by using a 2102 Dual-Probe Evaporimeter from Servo Med AB, Stockholm-Hasselby, Sweden as described elsewhere.⁽⁷⁻⁹⁾

3. Results and discussion

The vapour pressures over saturated aqueous solutions of potassium bromide, ammonium sulfate, copper(II) sulfate, iron(II) sulfate, and manganese(II) dichloride as a function of temperature are presented in table 1 and plotted in figures 1 to 5. They are reported together with corresponding results from the literature.^(2-6, 14, 15) There is a nice agreement between our and earlier works for CuSO_4 ,^(4, 6) FeSO_4 ,⁽⁴⁾ and $(\text{NH}_4)_2\text{SO}_4$,⁽³⁻⁵⁾ but our results are systematically slightly higher for KBr,^(4, 6) and MnCl_2 .^(4, 6, 15)

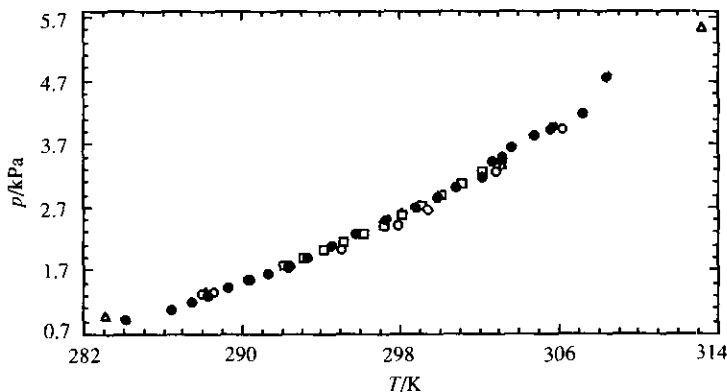


FIGURE 2. Vapour pressure of saturated $(\text{NH}_4)_2\text{SO}_4(\text{aq})$ as a function of temperature. □, Reference 3; ○, reference 4; △, reference 5; ●, this work.

TABLE 1. Vapour pressure p of saturated aqueous solutions

T/K	p/kPa	T/K	p/kPa	T/K	p/kPa	T/K	p/kPa	T/K	p/kPa
KBr(aq)									
284.28	0.973	289.83	1.553	295.05	1.969 ⁽⁴⁾	300.19	2.693	309.69	5.033
286.00	1.147	290.45	1.481 ⁽⁴⁾	295.20	2.146	302.85	3.132 ⁽⁴⁾		
287.89	1.413	292.35	1.669 ⁽⁴⁾	297.85	2.329 ⁽⁴⁾	303.35	3.433		
287.95	1.275 ⁽⁴⁾	292.48	1.766	298.48	2.560	306.25	3.810 ⁽⁴⁾		
289.60	1.467	293.15	1.746 ⁽¹⁴⁾	299.46	2.576 ⁽⁴⁾	308.37	4.700		
(NH ₄) ₂ SO ₄ (aq)									
283.15	0.972 ⁽⁵⁾	290.45	1.543 ⁽⁴⁾	295.05	2.041 ⁽⁴⁾	299.15	2.722 ⁽³⁾	303.15	3.362 ⁽⁵⁾
284.12	0.920	291.36	1.660	295.15	2.145 ⁽³⁾	299.45	2.669 ⁽⁴⁾	303.15	3.442 ⁽³⁾
286.45	1.087	292.15	1.773 ⁽³⁾	295.79	2.270	299.90	2.866	303.60	3.493
287.46	1.207	292.35	1.736 ⁽⁴⁾	296.15	2.281 ⁽³⁾	300.15	2.889 ⁽³⁾	304.83	3.830
287.95	1.319 ⁽⁴⁾	292.39	1.786	297.15	2.408 ⁽³⁾	300.85	3.000	305.58	3.920
288.15	1.355 ⁽⁵⁾	293.15	1.893	297.27	2.490	301.15	3.068 ⁽³⁾	305.69	3.973
288.31	1.303	293.15	1.896 ⁽⁵⁾	297.85	2.417 ⁽⁴⁾	302.14	3.177	306.25	3.942 ⁽⁴⁾
288.55	1.363 ⁽⁴⁾	293.37	1.916	298.15	2.600	302.15	3.256 ⁽³⁾	307.17	4.186
289.27	1.433	294.15	2.016 ⁽³⁾	298.15	2.568 ⁽⁵⁾	302.65	3.440	308.46	4.757
290.34	1.553	294.55	2.106	298.76	2.706	302.85	3.252 ⁽⁴⁾	313.15	5.755 ⁽⁵⁾
CuSO ₄ (aq)									
282.98	1.120	292.99	2.153	296.74	2.780	300.04	3.353	303.94	4.360
285.90	1.333	293.25	2.273 ⁽⁴⁾	297.31	2.866	300.75	3.534 ⁽⁴⁾	304.15	4.332 ⁽⁴⁾
289.12	1.627	294.76	2.466	298.15	3.090 ⁽⁶⁾	301.25	3.658 ⁽⁴⁾	306.95	5.094 ⁽⁴⁾
291.25	1.936	294.92	2.473	298.35	3.092 ⁽⁴⁾	301.43	3.466		
292.15	2.133 ⁽⁴⁾	295.75	2.636 ⁽⁴⁾	299.27	3.206	303.22	3.953		
FeSO ₄ (aq)									
280.72	0.773	286.10	1.340	293.93	2.300	298.15	3.020 ⁽⁴⁾	304.96	4.413
280.87	0.787	288.46	1.613	294.12	2.360	298.41	3.180	305.05	4.497 ⁽⁴⁾
281.08	0.800	290.11	1.813	295.25	2.533	300.39	3.450		
281.16	0.807	291.75	2.069 ⁽⁴⁾	296.35	2.713 ⁽⁴⁾	300.45	3.470 ⁽⁴⁾		
282.26	0.920	292.09	2.073	296.45	2.800	302.22	3.693		
284.18	1.117	293.35	2.276 ⁽⁴⁾	296.60	2.826	302.85	3.962 ⁽⁴⁾		
MnCl ₂ (aq)									
280.43	0.493	286.99	0.960	294.40	1.444 ⁽⁴⁾	299.55	1.922 ⁽⁴⁾	307.35	2.922 ⁽⁴⁾
281.20	0.540	288.71	1.082	295.48	1.686	300.16	2.135	307.61	2.880
281.40	0.567	289.83	1.173	296.68	1.813	302.02	2.266	309.16	3.026
282.29	0.633	290.65	1.157 ⁽⁴⁾	296.85	1.653 ⁽⁴⁾	302.05	2.204 ⁽⁴⁾	310.36	3.160
283.78	0.747	290.98	1.267	298.15	1.780 ⁽⁶⁾	302.27	2.355		
284.41	0.773	292.45	1.400	298.15	1.783 ⁽¹⁵⁾	303.84	2.520		
285.69	0.880	292.85	1.316 ⁽⁴⁾	298.32	1.960	304.35	2.508 ⁽⁴⁾		
286.82	0.947	294.01	1.533	298.58	2.013	305.81	2.693		

Since the molar volumes of liquid water and salts are negligible compared with that of the water vapour, and the water vapour can be treated as a perfect gas, the Clausius-Clapeyron equation for saturated solution takes the form:⁽¹¹⁾

$$d \ln p/d(1/T) = -\Delta_{\text{vap}}H_m(T)/R, \quad (1)$$

where the slope of $\ln(p/kPa)$ against $(1/T)$ is related to the enthalpy change

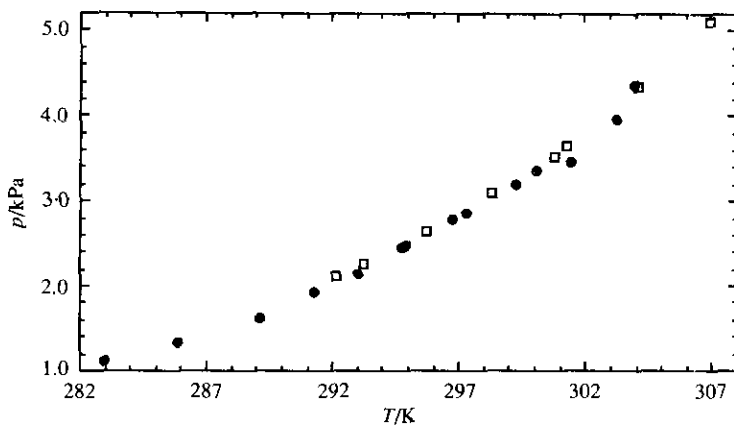


FIGURE 3. Vapour pressure of saturated $\text{CuSO}_4(\text{aq})$ as a function of temperature. \square , Reference 4; \bullet , this work.

$\Delta_{\text{vap}}H_m(T)$ associated with evaporating an amount of substance n_1 of water while simultaneously crystallizing an amount n_2 of salt.

Over a short range of temperatures, it can be assumed that $\Delta_{\text{vap}}H_m(T)$ varies linearly with temperature and therefore the integral form of the Clausius-Clapeyron equation can be written as

$$\ln(p/\text{kPa}) = A + B(T/\text{K})^{-1} + C \cdot \ln(T/\text{K}), \quad (2)$$

where the parameters A , B , and C (table 2) were evaluated using an unweighted multivariate least-squares method. For potassium bromide and manganese(II) dichloride vapour pressures determined only in this work were included in the calculations, while for ammonium sulfate, copper(II) sulfate, and iron(II) sulfate, all available vapour pressures were considered. In table 3 are presented, at 5 K intervals,

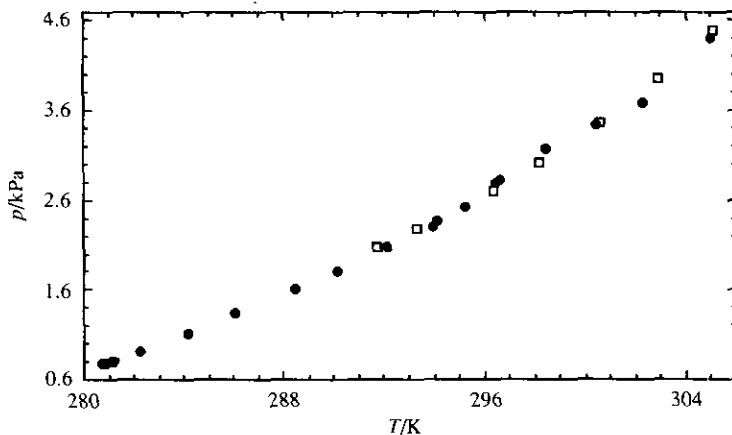


FIGURE 4. Vapour pressure of saturated $\text{FeSO}_4(\text{aq})$ as a function of temperature. \square , Reference 4; \bullet , this work.

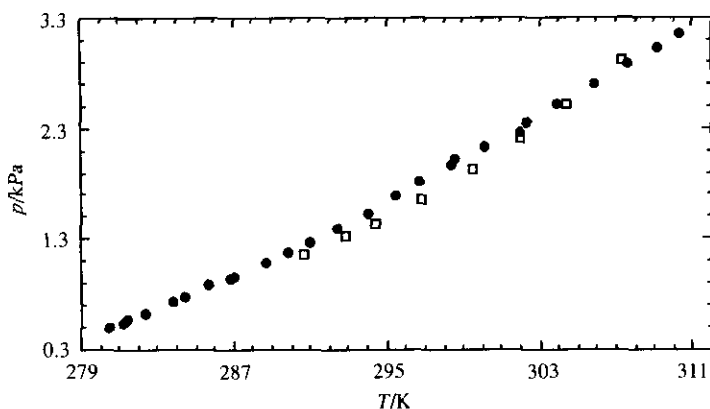


FIGURE 5. Vapour pressure of saturated $\text{MnCl}_2(\text{aq})$ as a function of temperature. \square , Reference 4; \bullet , this work.

the vapour pressures p ; activities of water: $a_1 = p/p_1$; osmotic coefficients: $\phi = -(\nu M_1 m_{\text{sat}})^{-1} \cdot \ln a_1$, and the enthalpies of vaporization: $\Delta_{\text{vap}} H_m(T)$. Here, M_1 is the molar mass of water and ν is the stoichiometric number of ions formed from the salt divided by the stoichiometric number of the salt. The vapour pressures p_1 of pure water at given T were calculated from the Saul and Wagner equation.⁽¹⁶⁾ The molality solubilities m_{sat} of salt in water as a function of temperature were taken from the Broul, Nývlt, and Söhnel tabulation.⁽¹⁷⁾

The solubility of salt hydrates having stoichiometric number h of H_2O as a function of temperature is given by⁽¹³⁾

$$\left\{ \partial \ln m / \partial (1/T) \right\} \left\{ \phi + m_{\text{sat}} (\partial \phi / \partial m)_T \right\} = -\Delta_{\text{sol}} H_m / \{ R(1 - h m_{\text{sat}} M_1) \}, \quad (3)$$

where $\Delta_{\text{sol}} H_m$ is the molar enthalpy of solution and R is the gas constant. Using the osmotic coefficients determined here, the solubility of salt in water⁽¹⁷⁾ and the change of osmotic coefficients with molality near saturation, the values of $\Delta_{\text{sol}} H_m$ can be calculated. These values can be compared with results of calorimetric measurements^(18,19) because

$$\Delta_{\text{sol}} H_m = \Delta_{\text{sol}} H_m^\infty - \Delta_{\text{dil}} H_m(m_{\text{sat}} \rightarrow 0), \quad (4)$$

TABLE 2. Parameters of equations (2)

Salt	A	B	C
KBr ^a	69.179	-7670.3	-7.4634
$(\text{NH}_4)_2\text{SO}_4^b$	458.77	-24980	-65.649
CuSO_4^b	137.65	-10705	-17.665
FeSO_4^b	1083.6	-52577	-159.04
MnCl_2^a	1270.0	-60386	-187.23

^a Only vapour pressures determined in this work are taken into account.

^b Calculated using all results from table 1.

TABLE 3. Solubilities, vapour pressures, water activities, osmotic coefficients, and molar enthalpies of vaporization as a function of temperature ($R = 8.3136 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)

$\frac{T}{\text{K}}$	$\frac{m_{\text{sat}}}{\text{mol} \cdot \text{kg}^{-1}}$ ^a	$\frac{p}{\text{kPa}}$	a_1	ϕ	$\frac{\Delta_{\text{vap}} H_m}{R \cdot \text{K}}$
KBr(aq)					
283.15	5.002	0.953	0.777	1.403	5557
288.15	5.237	1.338	0.785	1.282	5520
293.15	5.471	1.853	0.793	1.177	5482
298.15	5.703	2.533	0.800	1.087	5445
303.15	5.932	3.419	0.806	1.010	5408
308.15	6.157	4.563	0.811	0.942	5370
(NH ₄) ₂ SO ₄ (aq)					
283.15	5.494	0.901	0.734	1.041	6391
288.15	5.589	1.319	0.774	0.847	6063
293.15	5.688	1.871	0.801	0.747	5735
298.15	5.790	2.573	0.813	0.663	5407
303.15	5.896	3.439	0.811	0.659	5079
308.15	6.005	4.474	0.796	0.705	4750
CuSO ₄ (aq)					
283.15	1.055	1.113	0.907	2.565	5703
288.15	1.153	1.574	0.924	1.907	5615
293.15	1.260	2.189	0.937	1.439	5527
298.15	1.376	2.996	0.946	1.120	5438
303.15	1.502	4.037	0.952	0.917	5350
308.15	1.639	5.363	0.954	0.801	5262
FeSO ₄ (aq)					
283.15	1.352	0.978	0.797	4.655	7545
288.15	1.533	1.516	0.890	2.119	6750
293.15	1.729	2.208	0.945	0.911	5954
298.15	1.940	3.035	0.958	0.610	5159
303.15	2.165	3.950	0.931	0.918	4364
308.15	2.405	4.884	0.869	1.626	3569
MnCl ₂ (aq)					
283.15	5.421	0.697	0.568	1.931	7372
288.15	5.644	1.064	0.624	1.544	6437
293.15	5.884	1.515	0.648	1.363	5500
298.15	6.143	2.020	0.638	1.354	4563
303.15	6.422	2.535	0.597	1.484	3627
308.15	6.721	3.002	0.534	1.728	2691

^a Reference 17.

where $\Delta_{\text{dil}} H_m(m_{\text{sat}} \rightarrow 0)$ is the molar enthalpy of dilution of saturated solution and $\Delta_{\text{sol}} H_m^\infty$ is the molar enthalpy of solution at infinite dilution.

The osmotic coefficient of KBr(aq): $\phi(298.15 \text{ K}, m_{\text{sat}} = 5.70 \text{ mol} \cdot \text{kg}^{-1}) = 1.087$ is in a good agreement with other results: $\phi(298.15 \text{ K}, m_{\text{sat}} = 5.66 \text{ mol} \cdot \text{kg}^{-1}) = 1.047$,⁽²⁰⁾ and $\phi(298.15 \text{ K}, m_{\text{sat}} = 5.74 \text{ mol} \cdot \text{kg}^{-1}) = 1.033$.⁽²¹⁾ Introducing $d\phi/dm = 0.028 \text{ kg} \cdot \text{mol}^{-1}$,⁽²⁰⁾ into equation (3), the molar enthalpy of solution is: $\Delta_{\text{sol}} H_m(298.15 \text{ K}, m_{\text{sat}} = 5.70 \text{ mol} \cdot \text{kg}^{-1}) = 14.9 \text{ kJ} \cdot \text{mol}^{-1}$, a value close to the calorimetric

determinations: $(16.4 \text{ to } 16.5) \text{ kJ} \cdot \text{mol}^{-1}$,^(18, 19) and is consistent with $14.13 \text{ kJ} \cdot \text{mol}^{-1}$ from Pekárek and Vacek calculations.⁽²²⁾

The osmotic coefficients of $(\text{NH}_4)_2\text{SO}_4(\text{aq})$: $\phi(298.15 \text{ K}, m_{\text{sat}} = 5.0 \text{ mol} \cdot \text{kg}^{-1}) = 0.699$,⁽⁶⁾ $\phi(298.15 \text{ K}, m_{\text{sat}} = 5.84 \text{ mol} \cdot \text{kg}^{-1}) = 0.708$ ⁽²¹⁾ are close to our value: $\phi(298.15 \text{ K}, m_{\text{sat}} = 5.79 \text{ mol} \cdot \text{kg}^{-1}) = 0.663$. From $d\phi/dm = 0.026 \text{ kg} \cdot \text{mol}^{-1}$ ⁽⁶⁾ one has: $\Delta_{\text{sol}}H_m(298.15 \text{ K}, m_{\text{sat}} = 5.79 \text{ mol} \cdot \text{kg}^{-1}) = 6.5 \text{ kJ} \cdot \text{mol}^{-1}$. Only one result can be quoted from calorimetric measurements: $\Delta_{\text{sol}}H_m(293.15 \text{ K}, m = 0.555 \text{ mol} \cdot \text{kg}^{-1}) = 7.6 \text{ kJ} \cdot \text{mol}^{-1}$.⁽¹⁸⁾

Our osmotic coefficient of $\text{CuSO}_4(\text{aq})$: $\phi(298.15 \text{ K}, m_{\text{sat}} = 1.38 \text{ mol} \cdot \text{kg}^{-1}) = 1.12$, differs considerably from the isopiestic result: $\phi(298.15 \text{ K}, m = 1.40 \text{ mol} \cdot \text{kg}^{-1}) = 0.491$.⁽⁶⁾ The determined water activity is $a_1 = 0.946$ when the Robinson and Stokes value is $a_1 = 0.976$,⁽⁶⁾ (the difference in vapour pressures is about 0.09 kPa, when the bounds of experimental error are estimated to be about 0.01 kPa). Since the solid phase in equilibrium with the saturated solution was not identified in our study, possible explanation for lower vapour pressure can be associated with an incomplete conversion of used anhydrous copper(II) sulfate into pentahydrate. Using the Robinson and Stokes value of ϕ and $d\phi/dm = 0.09 \text{ kg} \cdot \text{mol}^{-1}$,⁽⁶⁾ the molar enthalpy of solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is $\Delta_{\text{sol}}H_m(298.15 \text{ K}, m = 1.40 \text{ mol} \cdot \text{kg}^{-1}) = 14.0 \text{ kJ} \cdot \text{mol}^{-1}$. Unfortunately, the calorimetric experiment was performed for a much lower molality: $\Delta_{\text{sol}}H_m(298.15 \text{ K}, m = 0.0416 \text{ mol} \cdot \text{kg}^{-1}) = 10.6 \text{ kJ} \cdot \text{mol}^{-1}$.⁽¹⁸⁾

Osmotic coefficients of $\text{FeSO}_4(\text{aq})$ are unknown in the literature. Using our result: $\phi(298.15 \text{ K}, m_{\text{sat}} = 1.94 \text{ mol} \cdot \text{kg}^{-1}) = 0.610$ and neglecting the term $d\phi/dm$ in equation (3), the molar enthalpy of solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is $\Delta_{\text{sol}}H_m(298.15 \text{ K}, m_{\text{sat}} = 1.94 \text{ mol} \cdot \text{kg}^{-1}) = 15.3 \text{ kJ} \cdot \text{mol}^{-1}$. Only the molar enthalpy of solution at infinite dilution is known: $\Delta_{\text{sol}}H_m^\infty = 11.8 \text{ kJ} \cdot \text{mol}^{-1}$.⁽¹⁸⁾

Osmotic coefficients of $\text{MnCl}_2(\text{aq})$: $\phi(298.15 \text{ K}, m_{\text{sat}} = 6.12 \text{ mol} \cdot \text{kg}^{-1}) = 1.741$,⁽²¹⁾ and $\phi(298.15 \text{ K}, m_{\text{sat}} = 6.09 \text{ mol} \cdot \text{kg}^{-1}) = 1.840$,⁽¹⁵⁾ differ from our value: $\phi(298.15 \text{ K}, m_{\text{sat}} = 6.14 \text{ mol} \cdot \text{kg}^{-1}) = 1.354$. Using ϕ from this work and $d\phi/dm = 0.0665 \text{ kg} \cdot \text{mol}^{-1}$,⁽¹⁵⁾ the molar enthalpy of solution of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ is: $\Delta_{\text{sol}}H_m(298.15 \text{ K}, m_{\text{sat}} = 6.14 \text{ mol} \cdot \text{kg}^{-1}) = 19.0 \text{ kJ} \cdot \text{mol}^{-1}$, but on introducing the Rard osmotic coefficient,⁽¹⁵⁾ the molar enthalpy of solution is $23.2 \text{ kJ} \cdot \text{mol}^{-1}$. Both values are close to the molar enthalpy of solution at infinite dilution: $\Delta_{\text{sol}}H_m^\infty = 18.9 \text{ kJ} \cdot \text{mol}^{-1}$.⁽¹⁸⁾

REFERENCES

1. Young, J. F. *J. Appl. Chem.* **1967**, 17, 241.
2. *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*. Washburn, E. W.: Editor. Vols 1 and 3. McGraw-Hill Book Co. Inc.: New York. **1926**.
3. Edgar, G.; Swan, W. O. *J. Am. Chem. Soc.* **1922**, 44, 570.
4. Diesnis, M. *Ann. Chemie* **1937**, 7, 5.
5. Adams, J. R.; Merz, A. R. *Ind. Eng. Chem.* **1949**, 41, 2013.
6. Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*. Butterworths: London. 2nd edition (revised). **1968**, p. 510.
7. Apelblat, A. *J. Chem. Thermodynamics* **1992**, 24, 619.
8. Apelblat, A. *J. Chem. Thermodynamics* **1993**, 25, 63.
9. Nilsson, G. E. *On the measurement of evaporative water loss. Methods and clinical applications*.

- Linköping Studies in Science and Technology Dissertations No. 11 and Linköping University Medical Dissertations No. 48, Linköping, 1977.
10. Hirschler, A. E. *J. Am. Chem. Soc.* **1936**, 58, 2472.
 11. Modell, M.; Reid, R. C. *Thermodynamics and Its Applications*. Prentice-Hall: Englewood Cliffs, NJ, 1974, pp. 338–339.
 12. Svoboda, V.; Pick, J. *Coll. Czechoslov. Chem. Commun.* **1979**, 43, 2973.
 13. Williamson, A. T. *Trans. Faraday Soc.* **1944**, 40, 421.
 14. Lescoeur, M. H. *Reserches sur la dissociation des hydrates salins et des composés analogues*. Thèse Doctorat des Sciences. Paris, 5 juin 1888 (quoted in reference 4).
 15. Rard, J. A. *J. Chem. Eng. Data* **1984**, 29, 443.
 16. Saul, S.; Wagner, W. *J. Phys. Chem. Ref. Data* **1987**, 16, 893.
 17. Broul, M.; Nývlt, J.; Söhnel, O. *Solubility in Inorganic Two-component Systems*. Elsevier: Amsterdam, 1981.
 18. Beggerow, G. *Heat of Mixing and Solution*. Hellwege, K. H.: editor. Landolt-Börnstein, New Ser. IV/2. Springer-Verlag: Berlin, 1976.
 19. Parker, V. B. *Thermal Properties of Aqueous Uni-univalent Electrolytes*. Nat. Bur. Stand. (U.S.): Washington, DC, 1965.
 20. Hamer, W. J.; Wu, Y.-C. *J. Phys. Chem. Ref. Data* **1972**, 1, 1047.
 21. Voznesenskaya, I. E. *Extended Tables of Activity and Osmotic Coefficients of Aqueous Solutions for 150 Electrolytes at 25 °C*. In *Problems of Physical Chemistry of Electrolyte Solutions* (in Russian). Mikulin, G. I.: editor. Khimiya: Leningrad, 1968, p. 172.
 22. Pekárek, V.; Vacek, V. *Industrial Crystallization 81*. Jančić, S. J.: editor. North-Holland: Amsterdam, 1982.