

A Thermodynamic Approach to the Measurement of Hygroscopicity

Aqueous Vapor Pressure of Univariant, Binary Systems, and Hygroscopicity Potential

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THE GENERAL CRITERION for equilibrium in a heterogeneous system at constant temperature and pressure stipulates the equality of chemical potential, u_i , of each component in every phase, P_x —i.e., $u_i(P_1) = u_i(P_2) = \dots = u_i(P_x)$. The univariant equilibria involving water and a soluble inorganic salt as components which are distributed through three phases are considered here. The systems of interest comprise a vapor phase and a saturated solution in contact with solid solute, and a vapor phase and a solid hydrate or anhydrous salt in contact with the next higher solid hydrate. The chemical potential of water, u_{H_2O} , in these systems is determined by the fugacity of the water vapor, f_{H_2O} —viz., $u_{H_2O} = RT \ln f_{H_2O} + \text{constant}$. At equilibrium under the relatively low pressure regime of ambient conditions, the fugacity of the water is substantially equal to the partial pressure of water in the vapor phase, and consequently, the fugacity is equal to the aqueous vapor pressure, p_{H_2O} ; thus, $u_{H_2O} = RT \ln p_{H_2O} + \text{constant}$.

If the vapor phase is considered to embrace the open, surrounding atmosphere, then for equilibrium to prevail, the partial pressure of water vapor in the air must be equal to the characteristic water vapor pressure or chemical potential of water of the binary system of interest at the temperature of observation. This condition establishes the thermodynamic basis or potential for the phenomena known as hygroscopicity and efflorescence (10). The driving force for the transfer of water to or from the condensed phases and the atmosphere is afforded by the difference between the chemical potential or partial pressure of water in the atmosphere, $p_{H_2O, \text{atm.}}$, and the chemical potential or aqueous vapor pressure of the binary system, $p_{H_2O, \text{sys.}}$. For positive values of $(p_{H_2O, \text{atm.}} - p_{H_2O, \text{sys.}})$ moisture absorption from the atmosphere or hygroscopicity will be observed; for negative values of the difference, moisture loss to the atmosphere or efflorescence in the instance of salt hydrates will occur.

An alternative method of expressing the above relations is to consider the equilibrium relative humidity of the system with respect to the existing relative humidity of the atmosphere. The effect of this approach is merely to multiply the difference $(p_{H_2O, \text{atm.}} - p_{H_2O, \text{sys.}})$ by the factor $100/p_{H_2O, \text{pure}}$.

The interaction of many materials with the moisture of the ambient atmosphere has been studied (1-3, 25, 26). These investigations have been spurred for the most part by the undesirable consequences occasioned in the application of highly hygroscopic and efflorescent substances. The use, handling, storage, shipping, and purity properties of many compounds alter with changes in water content. However, the assessment of interaction has not received consistent, systematic, and unambiguous treatment. This situation is due to a combination of two factors. One factor is related to a confusion between methods based on equilibrium considerations (the thermodynamic approach) and those effectively based on rate measurements (the kinetic approach); the other relates to the relative ease of obtaining experimental results.

To a great degree, the kinetic approach essentially has involved periodic, successive weighings of a test sample after exposure of the sample to an atmosphere of known moisture content at constant temperature (16). The results obtained through this technique are subject to many unassessable and uncontrollable variables—for example,

available surface area of sample, distribution of particle sizes in sample, geometrical configuration of sample, degree of air circulation through sample, degree of packing of sample, and existence and extent of possible induction periods. On occasion paradoxical results have been obtained in this laboratory from measurements of a kinetic type. For instance, coarse granules of a compound were considerably more hygroscopic over a short time interval than more finely divided material of far greater surface area under the same test conditions. This anomalous situation can be traced to more efficient circulation of moisture-laden air through the aggregates of coarse particles; the more densely packed, finer grains presented a good barrier to air circulation, so that diffusion of moisture through the liquid phase formed on the crystal surfaces became the primary means for contact of the salt below the sample surface with water.

The thermodynamic approach to water vapor-salt interaction is not beset by ambiguities due to unknown or difficultly measurable kinetic variables. Rather, determination of equilibrium water vapor pressures over a range of temperatures allows one to delineate with considerable accuracy the hygroscopicity limits of any water-soluble anhydrous or hydrated salt. Nevertheless, the manipulative ease of weighing has furthered use of the less well-defined kinetic approach. Measurements of the aqueous vapor pressures of binary systems, though achievable by many established methods (17, 21), cannot usually be performed on a perfunctory, routine basis without appreciable time, training, and acquired skill. Accordingly, this paper implements the thermodynamic method of hygroscopicity measurement by describing a relatively simple, direct, and specific means of moderate accuracy for determining aqueous vapor pressures.

The experimental technique applied by the present authors is based on the use of the Dunmore type of electric hygrometer (7, 8). This method stems from the calibrated change in the resistance of a thin film of electrolyte when the film is exposed to atmospheres of varying moisture contents (24). With the Dunmore-type element, the water vapor-sensitive unit consists of a thin film of lithium chloride deposited on a nonconductive plastic substrate between a bifilar winding of palladium wire. Measurement of the current through the element at a constant applied voltage affords a measure of the resistance of the element and, thereby, the moisture content of the atmosphere.

It is proposed here to choose as the criterion for hygroscopicity the negative value of the free energy change $(-\Delta F, \text{kcal. per mole})$ occasioned by the isothermal transfer of one mole of water vapor at the vapor pressure of pure water, $p_{H_2O, \text{pure}}$, to the aqueous vapor pressure of the univariant binary system of interest, $p_{H_2O, \text{sys.}}$. This value of $-\Delta F$ is termed the "hygroscopicity potential" (HP), and it is given by the relationships, $HP = -\Delta F = u_{H_2O, \text{pure}} - u_{H_2O, \text{sys.}} = RT \ln (p_{H_2O, \text{pure}}/p_{H_2O, \text{sys.}}) = 2.303RT \log_{10} (p_{H_2O, \text{pure}}/p_{H_2O, \text{sys.}})$, where R is the gas constant equal to 1.987 cal. per mole $^\circ K.$, and T is in $^\circ K.$ In this manner, the direct relation between the tendency to hygroscopic behavior and the imbalance in chemical potential of water in the ambient atmosphere and in the system is emphasized. The concept of hygroscopicity potential can be generalized still further, to allow computation of the free energy change

accompanying the transfer of water vapor under any set of experimental conditions. Hygroscopicity can be anticipated for positive HP values, loss of water to the atmosphere for negative HP values, and no transfer of water for $HP = 0$.

For many materials (9) the rate at which moisture is absorbed is claimed to be proportional to the difference ($p_{H_2O, atm.} - p_{H_2O, sys.}$). Consequently, the thermodynamic measurements will probably allow some insight into the rate processes involved, particularly where saturated solutions are formed. However, nucleation phenomena undoubtedly will complicate the kinetic behavior of systems of solid hydrate salts (11, 13, 14).

In summary, hygroscopicity may be viewed as a type of chemical reaction. Like all chemical reactions, it is characterized by a thermodynamic driving force and a kinetic rate. Measurements of the aqueous vapor pressure of a univariant salt-water system provide the fundamental thermodynamic data to determine whether a material, given sufficient time, will be hygroscopic at a particular $p_{H_2O, sys.}/p_{H_2O, atm.}$ ratio. For values of the ratio less than one, the rate at which atmospheric water is absorbed is dependent on many factors. The individual effects of these variables are usually unresolved in the customary kinetic experiment. As a consequence, the kinetic results are very sensitive to the physical circumstances of the material and cannot be extrapolated reliably to other experimental conditions.

EXPERIMENTAL

Equipment and Procedures. Relative humidity measurements were made using the appropriate sensing elements selected from a complete set of narrow-range, high-sensitivity Dunmore-type sensors (catalog numbers 4-4823, 4-4812, 4-4814, Hygro Dynamics Corp., Silver Spring, Md.), in conjunction with a 110-volt, alternating current, line-operated electric hygrometer indicator (catalog number 15-3000, Hygro Dynamics Corp.). The readings taken from the indicator were converted into relative humidity values by reference to the calibration charts furnished with each element. The calibration curves are given as functions of temperature, generally at 40°, 60°, 80°, 100°, and 120° F. Thus, temperature control of the test sample is required.

The test sample was thermostated by placing the sample in a wide-mouthed, unsilvered Dewar-type flask with upper and lower side arms, so that tempered water could be circulated from a constant temperature bath reservoir. In this fashion, the temperature of the test system could easily be maintained to within 0.1° C. For samples of salt solutions, the flask was held vertically and a magnetic stirrer was used to hasten establishment of equilibrium. For samples of solids, the flask was inclined somewhat and the salts were spread over the inner surface of the flask to expose a large portion of the crystal surfaces. In both instances, the sensing element was led into the flask through a tightly fitting rubber stopper and was thus suspended by the electrical cable above the sample. Attainment of equilibrium was judged by the constancy of the relative humidity readings over successive 4-hour periods. Reproducible results could be obtained only by the passage of electric current through the element at the time of observation. Apparently, continuous current flow through the element results in spurious readings caused by its resistive heating.

All relative humidity readings were converted to actual values of $p_{H_2O, sys.}$ (in millimeters of mercury). For subsequent comparative purposes the average value for the heat of vaporization of water over the temperature range of 40° to 120° F. was obtained from a plot of handbook data (12). This value is 10,495 cal. per mole or 583.1 cal. per gram of water, and the corresponding vapor pressure equation is given by $\log_{10} p_{H_2O, pure} = -2293.5/T + 9.0648$.

Because of the fairly short temperature interval covered in the present work, the integrated form of the Clapeyron-Clausius equation, $\log_{10} p_{H_2O, sys.} = -\Delta H_{vap.}/2.303RT +$

constant, was found to represent adequately the experimental data reported below.

Assessment of Applicability of Method. To check the suitability of the electric hygrometer, the aqueous vapor pressures of several previously reported systems were determined. Table I shows the data for a 25 weight % solution of sodium chloride in water compared with similar data (23). The aqueous vapor pressure corresponding to the equilibrium $CuSO_4 \cdot 5H_2O(s) \rightleftharpoons CuSO_4 \cdot 3H_2O(s) + 2H_2O(g)$ was also determined. A mixture of the two solid hydrates containing 25.4% $CuSO_4 \cdot 3H_2O$ and 74.6% $CuSO_4 \cdot 5H_2O$ (as determined by thermogravimetry) was prepared by partial dehydration of the pentahydrate salt. After dehydration, the mixture of hydrates was tumbled in a ball mill for several days to ensure equilibration. From the linear plot of $\log_{10} p_{H_2O, sys.}$ against $1/T$, the heat of dissociation of the pentahydrate per mole of water vaporized, was found to be 13,161 cal. per mole compared with the reported value of 13,204 cal. per mole (5).

Hygroscopicity Potentials. POTASSIUM PERCHLORATE-WATER SYSTEM. The hygroscopicity potential of potassium perchlorate was computed after measurement of the aqueous vapor pressure of its saturated solutions in water over the temperature range of 40° to 120° F. (Table II,A). From a plot of these data, the equation $\log_{10} p_{H_2O, sys.} = -2259.2/T + 8.9106$ held over the temperature range cited.

The low values for the difference ($p_{H_2O, pure} - p_{H_2O, sys.}$) attest to the very low tendency toward hygroscopicity of potassium perchlorate and indicate that the salt may be exposed to humidities as high as 95% of saturation without moisture absorption from 40° to 100° F.

SODIUM PERCHLORATE-WATER SYSTEMS. Sodium perchlorate forms a monohydrate which has a transition temperature at about 51° C. (6). Accordingly, moisture pickup by sodium perchlorate will first engender monohydrate formation, followed by formation of a saturated solution of the monohydrate. The monohydrate is stable up to the highest temperature in this study (120° F. or 48.9° C.).

The results for the equilibrium $NaClO_4 \cdot H_2O(s) \rightleftharpoons NaClO_4(s) + H_2O(g)$ are tabulated in Table II,B. The test sample consisted of a mixture of 36.3% $NaClO_4$ and 63.7% $NaClO_4 \cdot H_2O$ obtained by partial hydration of the anhydrous salt. Perchlorate analyses were used to determine the composition of the salt mixture (22). The vapor pressure equation derived from the data of Table II,B, is given by $\log_{10} p_{H_2O, sys.} = -2615.1/T + 9.5923$, with a heat of vaporization corresponding to 11,967 cal. per mole of water. On the basis of this enthalpy value, the heat of formation of sodium perchlorate monohydrate is -162.0 kcal. per mole, which compares favorably with -162.5 kcal. per mole derived from the calorimetric data of Smeets (20).

The data for saturated solutions of sodium perchlorate monohydrate are given in Table II,C. The fact that the vapor pressures of the saturated solutions are consistently higher than those of the anhydrous salt-monohydrate mixture shows that the anhydrous salt will first be converted to the monohydrate before solution formation ensues. The data of Table II,C, are represented by the equation $\log_{10} p_{H_2O, sys.} = -2086.6/T + 8.0136$.

LITHIUM PERCHLORATE-WATER SYSTEMS. A phase study of the binary system $LiClO_4 \cdot H_2O$ (19) shows the occurrence of a monohydrate and a trihydrate salt with transition temperatures of 92.5° and 145.8° C., respectively. Thus, the systems $LiClO_4(s) - LiClO_4 \cdot H_2O(s) - H_2O(g)$, $LiClO_4 \cdot H_2O - LiClO_4 \cdot 3H_2O(s) - H_2O(g)$, and $LiClO_4 \cdot 3H_2O(s) - saturated\ solution - H_2O(g)$ were studied to define the hygroscopicity limits.

A mixture of 50.9% $LiClO_4 \cdot H_2O$ and 49.1% $LiClO_4$ was prepared by partial hydration of anhydrous lithium perchlorate. A mixture of 72.0% $LiClO_4 \cdot 3H_2O$ and 28.0% $LiClO_4 \cdot H_2O$ was prepared by partial dehydration of lithium perchlorate trihydrate. Both mixtures were

tumbled in a ball mill for 2 days prior to use. In each instance the distribution of hydrate salts was determined from the over-all perchlorate anion content (22).

No vapor pressure readings could be obtained with the $\text{LiClO}_4(\text{s})-\text{LiClO}_4\cdot\text{H}_2\text{O}(\text{s})-\text{H}_2\text{O}(\text{g})$ system with the present equipment, even at the highest temperature studied, 140° F. Thus, the aqueous vapor pressure over this system at 140° F. must be below about 1.5 mm. of mercury and at 40° F., below about 0.06 mm. Consequently, the hygroscopicity potential of this system is very high.

Only two readings could be recorded for the $\text{LiClO}_4\cdot\text{H}_2\text{O}(\text{s})-\text{LiClO}_4\cdot 3\text{H}_2\text{O}(\text{s})-\text{H}_2\text{O}(\text{g})$ system with the electric hygrometer. At 80° and 140° F. vapor pressures corresponding to 0.51 and 7.92 mm. of mercury, respectively, were recorded. These data gave the approximate equation $\log_{10} p_{\text{H}_2\text{O, sys.}} = -3563.3/T + 11.592$ with a value of 16.3 kcal. per mole of water vaporized. An approximate value for the heat of formation of lithium perchlorate monohydrate could then be computed on the basis of the reaction: $\text{LiClO}_4\cdot 3\text{H}_2\text{O}(\text{s}) \rightarrow \text{LiClO}_4\cdot\text{H}_2\text{O}(\text{s}) + 2\text{H}_2\text{O}(\text{g})$, $\Delta H = 32.6$ kcal. Appropriate complementary data (15, 18) yielded a value of -310.8 kcal. per mole for the heat of formation

of lithium perchlorate trihydrate. A value of -163 kcal. per mole was thus obtained for the heat of formation of lithium perchlorate monohydrate.

The vapor pressure data for saturated solutions of lithium perchlorate trihydrate (Table III,A) yield the equation $\log_{10} p_{\text{H}_2\text{O, sys.}} = -1984.2/T + 7.8537$ with a value of 504 cal. per gram of water vaporized. The somewhat higher value of vaporization of pure water when compared to the above value for the system over the same temperature range (583 vs. 504 cal. per gram) is a reflection of the endothermic solution process for lithium perchlorate trihydrate (15, 20). Energy absorption during dissolution is reclaimed upon evaporation of water and exothermic crystallization of salt.

Vapor pressure values for an unsaturated solution containing 15 weight % lithium perchlorate are listed in Table III,B. These data are represented by the equation $\log_{10} p_{\text{H}_2\text{O, sys.}} = -2333.3/T + 9.1379$, where the heat of vaporization of water is 593 cal. per gram. The somewhat higher value of the heat of vaporization of water from the unsaturated solution in comparison to that of pure water is indicative of the extensive solution or hydration of the lithium ion (4).

Table I. Aqueous Vapor Pressure (Millimeters of Mercury)

Temp., ° F.	25 Wt. % NaCl in Water		$\text{CuSO}_4\cdot 5\text{H}_2\text{O}(\text{s})-\text{CuSO}_4\cdot 3\text{H}_2\text{O}(\text{s})-\text{H}_2\text{O}(\text{g})$ System	
	$p_{\text{H}_2\text{O, sys.}}$, exptl.	Lit. (23)	$p_{\text{H}_2\text{O, sys.}}$, exptl.	Lit. (5)
40	4.6	4.8
60	9.8	10.3	3.7	3.8
80	19.8	20.4	8.4	8.9
100	37.9	38.1	18.4	19.5
120	68.5	68.4	39.6	41.0

Table II. Aqueous Vapor Pressure (Millimeters of Mercury)

Temp., ° F.	$p_{\text{H}_2\text{O, pure}}$	$p_{\text{H}_2\text{O, sys.}}$	$\Delta p_{\text{H}_2\text{O}}$	HP, Kcal. per Mole
40	6.3	5.9	0.4	0.036
60	13.3	12.7	0.6	0.027
80	26.2	25.0	1.2	0.028
100	49.0	46.1	2.9	0.038
120	87.8	78.7	9.1	0.070
B. System $\text{NaClO}_4\cdot\text{H}_2\text{O}(\text{s})-\text{NaClO}_4(\text{s})-\text{H}_2\text{O}(\text{g})$				
40	6.3	1.5	4.8	0.79
60	13.3	3.0	10.3	0.85
80	26.2	7.7	18.5	0.73
100	49.0	15.4	33.6	0.72
120	87.8	29.7	58.1	0.69
C. Saturated Solutions of $\text{NaClO}_4\cdot\text{H}_2\text{O}$				
40	6.3	3.2	3.1	0.37
60	13.3	6.2	7.1	0.44
80	26.2	11.6	14.6	0.49
100	49.0	21.2	17.8	0.52
120	87.8	34.3	53.5	0.60

Table III. Aqueous Vapor Pressure (Millimeters of Mercury)

Temp., ° F.	$p_{\text{H}_2\text{O, pure}}$	$p_{\text{H}_2\text{O, sys.}}$	$\Delta p_{\text{H}_2\text{O}}$	HP, Kcal. per Mole
40	6.3	5.1	1.2	0.12
60	13.3	9.5	3.8	0.19
80	26.2	17.4	8.8	0.24
100	49.0	31.2	17.8	0.28
120	87.8	49.3	36.5	0.36
B. 15 Weight % Solution of Lithium Perchlorate Trihydrate in Water				
40	6.3	5.4	0.9	
60	13.3	11.8	1.5	
80	26.2	24.0	2.2	
100	49.0	44.1	4.9	
120	87.8	78.1	9.7	

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