e-PS, 2009, **6**, 122-128 ISSN: 1581-9280 web edition ISSN: 1854-3928 print edition

www.Morana-rtd.com © by M O R A N A RTD d.o.o.







FULL PAPER

TEMPERATURE AND HUMIDITY CONSIDERATIONS FOR THE PRESERVATION OF ORGANIC COLLECTIONS - THE ISOPERM REVISITED

Tom Strang, David Grattan

Canadian Conservation Institute Department of Canadian Heritage 1030 Innes Rd., Ottawa, Ontario Canada K1A0M5

corresponding author: Tom.Strang@pch.gc.ca

Since Sebera published his paper on Isoperms in 1994, much has changed. A significant amount of data has accumulated on the mechanism of paper degradation, more activation energies have been determined and there has been a convergence of values. Assumptions about the relationship between the relative humidity and the moisture content or the rate of degradation of paper need no longer be made as near complete theoretical descriptions are available. The method of modelling has therefore been revised and now incorporates the Arrhenius equation and the moisture sorption isotherm, which is best modelled by the Guggenheim-Anderson-deBoer (GAB) equation. This new method will allow direct experimental verification of the isoperm for cellulosic materials in museum collections. As the cost of energy usage for preservation has now become an important question, it is particularly critical to have access to more accurate isoperms.

1 Introduction

The following argument is based on the notion that it is the concentration of water in the cell wall of the paper fibres (where the chemical processes of deterioration actually occur) rather than the concentration of water vapour in the atmosphere (the RH), which has a direct impact on the rate of degradation of paper. In the conventional understanding of reaction kinetics it is concentration of reactant which controls rate of reaction, hence it would be surprising, if a parameter which is only indirectly related to reactant concentration i.e. RH had a simple direct controlling influence on rate of reaction - i.e. degradation. This assumption that moisture content - which expresses the water concentration in the cell wall - has a direct controlling influence has been used in CCI's approach to accelerated ageing for paper for some time now, and we have used constant moisture content rather than constant relative humidity at all elevated temperatures in our ageing protocols. We support this notion in two ways - one is that there is evidence of the direct relationship with moisture content in

received: 29.10.2008 accepted: 15.05.2009

key words:

Kinetics, Arrhenius equation, mixed-control, paper degradation, accelerated ageing, Guggenheim - Anderson - deBoer

the work of Zou, Uesaka and Gurnagul¹. Their data is plotted in Figure 1 below to demonstrate this relationship.

The second point is that even if some may consider that the evidence is indecisive on whether it is RH or moisture content which has a direct controlling influence on reaction rate - we should at the very least calculate the isoperms for both situations.

Sebera proposed the isoperm² as a quantitative tool for predicting "preservation outcome" as part of a greater preservation strategy for protecting collections of paper. His Isoperm plot is shown in Figure 2.

The isoperm is a line of constant permanence (or deterioration rate) on a graph of humidity versus temperature. The line that runs through the standard museum set point at 50% RH and 20°C is arbitrarily set at unity, as the reference line, and other lines are established relative to this at half or double the permanence etc.

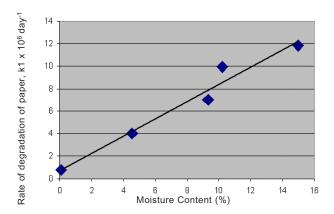


Figure 1: The rate of deterioration of paper versus moisture content Zou, Uesaka and Gurnagul data.¹

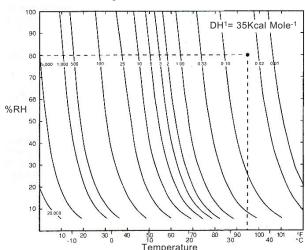


Figure 2: Sebera isoperm as a quantitative tool for predicting "preservation outcome".

Thus at a glance the impact of altering the conditions on degradation can be determined. This approach has been applied by others to paper and to other materials for which deterioration rates have been determined, such as cellulose acetate film stock (Riley, Image Permanence Institute - IPI³). All except the IPI method have assumed simple proportionality between degradation rate and relative humidity as did Sebera and thus all their predictions about rate must be open to question. The IPI method, unfortunately, remains somewhat opaque, as the derivation has not been published.

Sebera expresses the isoperm through this equation where:

$$\frac{P_2}{P_1} = \frac{r_1}{r_2} = \frac{RH_1}{RH_2} = \frac{MC_1}{MC_2} \tag{1}$$

P is the symbol for *permanence*, the inverse of deterioration rate

r is the *deterioration rate*, a measurable rate of loss of a key property

RH is the *relative humidity* of storage or display MC is the *moisture content* of the stored paper *subscript* 1 represents the initial or reference state *subscript* 2 represents a proposed state for comparison

For the following discussion, water concentration in units of weight of water per unit weight of substrate has been replaced by the percent moisture content (MC) which has the same units x100. This substitution was carried out for reasons of convenience and because moisture content is a better known and more easily accessible parameter.

$$[H_2O] \propto MC$$

For convenience and clarity in the equations the water activity Aw which is equivalent to %RH/100 is used rather than relative humidity RH, and Sebera's rate terms r_1 , r_2 are substituted by the k_1 and k_2 , the symbols normally employed to express rate in kinetic expressions such as the Arrhenius equation.

Grattan noted⁴ that Sebera's assumption:

$$\frac{RH_1}{RH_2} = \frac{MC_1}{MC_2} \tag{2}$$

is not consistent with the sorption isotherm, because it describes a simple linear relationship, whereas it is very well established that the relationship is an "S" shaped curve. Linearity is only roughly approximate in the middle of the moisture sorption isotherms that characterize most structural organic materials. There is significant non-linearity at the dry and damp ends where the greatest protection and maximum deterioration occur.

The relationship is more properly described by MC = f(RH) or $[H_2O] = f(A_w)$. Many equations

have been proposed to describe this function⁵. After a review of sorption isotherms for paper products and applicable models, Parker et al.⁶ determined that the Guggenheim-Anderson-deBoer equation (GAB) was the most effective representation of paper moisture sorption. It is limited (less accurate) only where pore filling begins to dominate at a relative humidity in excess of 95%.

Real gains in preservation occur in cool dry conditions whereas the highest rate of loss is in a damp and warm environment. Modifying storage and display environments to extend object lifetime (to create what is often called a "stable environment") yields a cost or a benefit accrued over time, that is related to the degree of deviation from the climatic norm. The isoperm thus needs to be recalculated in light of its potential influence in stipulating environmental standards for preservation, and particularly in balancing energy efficient building design with collections care. To do so will call on the best knowledge of paper permanence and challenge our lack of knowledge about thermal deterioration rates in many materials besides paper found in collections.

Zou et al.¹ reviewed the literature and showed experimental evidence to support a linear relationship between moisture content (n.b. <u>not</u> relative humidity) and a first order rate constant for the hydrolysis (or hydrolytic deterioration) reaction. So, for the isoperm model to estimate *permanence* (3) it must calculate a deterioration rate correlated to relative moisture contents of the reference state and the proposed state.

$$\frac{P_2}{P_1} = \frac{MC_1}{MC_2} \times \frac{k_1}{k_2} \tag{3}$$

It is an equation which, interestingly, is in partial agreement with Sebera's equation. However, environmental controls are specified in terms of temperature and relative humidity. To resolve this problem two equations are substituted into the model:

$$\frac{P_2}{P_1} = \frac{GAB_1}{GAB_2} \times \frac{k_1}{k_2} \tag{4}$$

The GAB equation to give moisture content:

$$M = \frac{M_o K C A_w}{(1 - K A_w)(1 - K A_w + C K A_w)}$$
 (5)

And the Arrhenius equation to provide k:

$$k = \mathcal{A} \exp \frac{-\mathcal{E}_a}{RT} \tag{6}$$

Where:

T is temperature (°K) ε_a activation energy (J/mol/°K) A is the pre-exponential or frequency factor R is the gas constant} 8.314 (J/mol/°K)

M is the equilibrium moisture content, dry basis M_o is the mono-layer moisture content K is the difference in state between pure liquid and upper layers

C is the difference in state between the monolayer and upper layers

Aw is the water activity

The Arrhenius contribution k_1/k_2 expands as:

$$\frac{k_1}{k_2} = \frac{\mathcal{A}_1}{\mathcal{A}_2} \times \frac{\exp\frac{-\mathcal{E}_a}{RT_1}}{\exp\frac{-\mathcal{E}_a}{RT_2}} \tag{7}$$

which can be represented as:

$$\frac{k_1}{k_2} = \frac{\mathcal{A}_1}{\mathcal{A}_2} \times \exp\frac{\mathcal{E}_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{8}$$

Pre-exponential factors (A values) are commonly considered as temperature independent and hence constant and thus could be cancelled. Even so, this constancy is always qualified as being for "small temperature" differences only, without "small" being properly characterized. From the original derivation of the Arrhenius model, A has been taken to represent the product of the number of activated molecules times the frequency of collision⁷. However, A is indicated to be mildly temperature sensitive⁸ as:

$$\mathcal{A} = 10^3 N_A (r_a + r_b)^2 \left(\frac{8\pi kT}{\mu}\right)^{\frac{1}{2}}$$
 (9)

where r_a and r_b are the radii of two spherical reactants.

This relationship implies, by collision theory, that A is proportional to \sqrt{T} but difficult to measure due to the "long extrapolation of the Arrhenius plot to 1/T = 0".8

It is easy to dismiss the possibility of A having a temperature dependence, because it might be considered that the practical storage temperature range may not prove enough to change the ratio of $A_1/A_{,2}$. However, the possibility exists that the A values are different. Zou et al. 9 redefine A as A_a which contains all the moisture related contributions to deterioration (see their section 2.1). As we are changing the moisture concentration, and there is a possibility $A_{1,2}$ could be determined with some precision 10 our model substitutes A_1/A_2 with GAB_1/GAB_2 to describe the influence of moisture in calculation of the isoperm.

Adding the Guggenheim, Anderson-deBoer (GAB) equation to relate relative humidity to moisture content gives the isoperm equation as: (10) where the fixed parameters are:

 P_1 the permanence, set as 1 "lifetime

$$\frac{P_2}{P_1} = \frac{\frac{M_{o1}K_1C_1A_{w1}}{(1-K_1A_{w1})(1-K_1A_{w1}+C_1K_1A_{w1})}}{\frac{M_{o2}K_2C_2A_{w2}}{(1-K_2A_{w2})(1-K_2A_{w2}+C_2K_2A_{w2})}} \times \exp\frac{\mathcal{E}_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\frac{P_2}{P_1} = \left(\frac{RH_1}{RH_2}\right) \left(\frac{T_1 + 460}{T_2 + 460}\right)^{10^{394\Delta H^{\ddagger}} \left(\frac{1}{T_2 + 460} - \frac{1}{T_1 + 460}\right)}$$
(11)

 A_{w1} the water activity set to 0.50 (50% RH as p_o/p_i) T_1 set to 293.15 °K (20 °C)

 ϵ_a set to the activation energy of the material (J/mol/ $^{\circ}K)$

R the gas constant, is 8.314 (J/mol/°K)

 M_{o1} is the material's GAB monolayer moisture constant at 20 °C, 50% RH

 K_1 is the material's pure liquid to upper-layer GAB parameter (20 °C, 50% RH)

 C_1 is the material's monolayer to upper-layer GAB parameter (20 °C, 50% RH)

And solving for A_{w2} in each case with the variables:

 T_2 set to the comparison temperature (°K)

 M_{o2} from the GAB fit of the sorption isotherm at T_2 K_2 ditto

C₂ ditto

P2 set to the desired 'lifetime multiplier"

The isoperms can be calculated by incrementing or decrementing the ratio P_2/P_1 (the lifetime multiplier) in integral units such as by two or three or by half etc. where P_1 is set to unity, and solving for A_{w2} . This humidity value is then checked against the GAB equation's limits of reasonable application: (0 < A_{w2} > 0.95), and plotted if it is within bounds. Once the search along the isotherm is exhausted we change to a new temperature T_2 and matching isotherm.

To carry out this work over a significant area, each material requires a family of sorption isotherms from 0.0 to 0.95 A_w , and deterioration rate data.

The newly proposed isoperm model is a function of the Arrhenius and GAB equation parameters:

$$A_{w2}$$
=function(e_a , T_1 , T_2 , A_{w1} , M_{o1} , K_1 , C_1 , M_{o2} , K_2 , C_2 , P_1 , P_2)

As an example calculation, the reference point for permanence is P_2/P_1 = 1 at T_1 = 20 °C and A_{w1} = 0.5 which requires:

$$GAB_1 = f(T_1, A_{w1}, M_{o1}, K_1, C_1)$$

where A_{w1} defines the point on the reference isotherm curve for T_1 . The comparison point is defined as the series of positive fractions (isoperms) P_2/P_1 which lie on the isotherm:

$$GAB_2 = f(T_2, M_{o2}, K_2, C_2)$$

 A_{w2} is the unknown to be calculated from a derivation of the revised isoperm equation (4) at the specified P_2/P_1 . Any A_{w2} value outside the validity

range (0 < A_w > 0.95) for the GAB₂ equation is discarded.

For comparison, Sebera's combined equation for the isoperm is (11) uses the Eyring term for which there is no data available instead of the Arrhenius relationship for which a significant amount of experimental data exists. To quote Sebera: "these equations can be evaluated algebraically to obtain a quantitative evaluation of permanence changes". (Note that Sebera's temperature is in Fahrenheit units).

2.1 Derivation of isoperms from Zou et al. paper degradation model

Isoperms can also be derived from Zou et al.'s model^{1,9}. Using Zou et al.'s equation (12) directly builds on the Arrhenius data by partitioning the pre-exponential factor into several influences: oxidative reactions, water, and pH, and denoting this expansion as

$$A_a = A_{a0} + A_{a2}[H_2O] + A_{a5}[H^+][H_2O]$$
 (12)

where:

 A_{a0} is non-moisture, non acidity related degradation, $4.54 \times 10^9 \text{ day}^{-1}$

 A_{a2} water concentration/moisture content related degradation, 2.83 x10¹² day⁻¹

 A_{a5} acidity related degradation, 9.85 x 10¹⁶ Lmol⁻¹ day⁻¹

The relative importance of these is dealt with in Zou et al.⁹ further reducing equation (12) to:

$$\mathcal{A}_a = \mathcal{A}_{a0} + \mathcal{A}'_{a2}[H_2O] \tag{13a}$$

where:

$$\mathcal{A}'_{a2} = \mathcal{A}_{a2} + \mathcal{A}_{a5}[H^+] \tag{13b}$$

If we substitute the GAB equation into the water concentration term $[H_2O]$ of equation (13a), the resulting A_a factor can be interpreted in terms of water activity A_w (and thus RH) and allow predictions to be made for the effect of storage RH as originally intended by Sebera's isoperm model. The relationship so derived is thus consistent with current deterioration theory, based on tested Arrhenius principles, and on empirical data from well understood procedures.

It can be safely assumed that the non-moisture related, non hydrolytic pH influenced oxidation and

starting [H+] terms are equal for reference and comparison condition, they can be ignored and the resultant model becomes similar in form to new isoperm model proposed above in equation (10) as well as retaining most of the fractional A_w value (Zou et al.'s A_{a0} is 1000 times less than A_{a2}).

The permanence ratio is given in equation (14) which is a restatement of equation (4).

$$\frac{P_2}{P_1} = \frac{GAB_1}{GAB_2} \exp \frac{\mathcal{E}_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \tag{14}$$

As discussed by Zou et al.9, the moisture driven hydrolysis reaction as described by A_{a2} is generally the greater contributor of the three A_a terms, and specifically so in alkaline conditions. We could then argue the other terms could be ignored outright. However there is a caveat by which we would expect the new model (14) to be an overestimate of permanence. This equation reflects the 'start condition' only, and does not integrate changes during ageing. In non-alkaline papers we expect pH shift during ageing, approximately one pH point or tenfold [H+] increase, which would decrease permanence in the moister comparison samples (P. Bégin, pers. com.).

The complete definition following from Zou et al.'s equation retaining the significant terms from equation (12) is presented in equation (15).

After reviewing the sources, we can modify either the Sebera or Zou et al. models in similar fashion to properly describe the isoperm.

2.2 Finding the solution to the **Grattan-Strang model**

To derive an equation for A_{w2} that can be calculated, we continue with equation (14) (see equations 16 to 18).

To ease manipulation we can symbolize the ratios of fixed values and other segments.

Where:

The GAB parameter ratio

$$S_{1,2} = \frac{M_{o1}K_1C_1}{M_{o2}K_2C_2}$$

The GAB₁ denominator is $gab_1 = (1-K_1A_{w1})(1-K_1A_{w1}+C_1K_1A_{w1})$ The GAB2 denominator is $gab_2 = (1-K_2A_{w2})(1-K_2A_{w2}+C_2K_2A_{w2})$

Applying the symbolic representation gives:

$$\frac{P_2}{P_1} = \mathcal{S}_{1,2} \times \frac{A_{w1} \times gab_2}{A_{w2} \times gab_1} \times arr_{1,2} \qquad \textbf{(19)}$$

Rearrangement to put the two terms containing Aw2 together gives:

$$\frac{A_{w2}}{gab_2} = S_{1,2} \times \frac{A_{w1}}{gab_1} \times arr_{1,2} \times \frac{P_1}{P_2}$$
 (20)

As they are all known quantities for the purpose of a single calculation, the right hand side can be reduced to a constant:

$$\mathcal{N} = \mathcal{S}_{1,2} \times \frac{A_{w1}}{gab_1} \times arr_{1,2} \times \frac{P_1}{P_2}$$
 (21)

The full isoperm equation becomes:

$$\frac{A_{w2}}{gab_2} = \mathcal{N} \tag{22}$$

Rearranging:

$$0 = \frac{A_{w2}}{gab_2} - \mathcal{N}$$
 (23)

$$0 = A_{w2} - \mathcal{N} gab_2$$
 (24)

$$0 = A_{w2} - \mathcal{N} gab_2 \tag{24}$$

Rearranging terms to solve for A_{w2} (see equations 25 to 31) and setting constants:

$$\alpha = K_2^2 (1 - C_2)$$

 $\beta = (C_2 K_2 - 2K_2 - 1/\mathcal{N})$
 $\gamma = 1$

Substituting α , β and γ reveals the quadratic:

$$0 = \alpha A_{w2}^2 + \beta A_{w2} + \gamma \tag{32}$$

Taking the roots of the quadratic yields:

$$A_{w2} = \frac{-\beta \pm \sqrt{\beta^2 - 4\alpha\gamma}}{2\alpha} \tag{33}$$

Back substitution of α , β and γ in equation (33) yields equation (34), providing a solution of the Isoperm in water activity units where water activity is equal to %RH/100 or the relative moisture vapour pressure. Below 50 °C the deviation of water activity from this definition is less than 0.2 % from actual measurements. 11,12

3 Conclusion

The evidence supporting our approach to modelling the isoperm hinges on a linear relationship based on five data points in Zou et al.1 At present this is only confirmed for 90 degree centigrade exposure. However, from a qualitative standpoint it is logical that the moisture in the cell wall (rather than in the air) will be rate determining. This being the case, it is necessary to examine the situation by employing a more likely relationship between moisture content and degradation. Our model corrects Sebera's simplifying assumption that RH₁/RH₂=MC₁/MC₂ and directly represents the measured concentration of water. And this is not just an academic question because current RH guidelines for museums and archives are based on Sebera's calculation. We need therefore to examine the impact of making a more likely assumption

$$\frac{P_2}{P_1} = \frac{\mathcal{A}_{0_1} + \mathcal{A}_{a2_1}GAB_1 + \mathcal{A}_{a5_1}[H^+]GAB_1}{\mathcal{A}_{0_2} + \mathcal{A}_{a2_2}GAB_2 + \mathcal{A}_{a5_2}[H^+]GAB_2} \times \exp\frac{\mathcal{E}_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$
(15)

$$\frac{P_2}{P_1} = \frac{\frac{M_{o1}K_1C_1A_{w1}}{(1-K_1A_{w1})(1-K_1A_{w1}+C_1K_1A_{w1})}}{\frac{M_{o2}K_2C_2A_{w2}}{(1-K_2A_{w2})(1-K_2A_{w2}+C_2K_2A_{w2})}} \times \exp\frac{\mathcal{E}_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$
(16)

$$\frac{P_2}{P_1} = \frac{M_{o1}K_1C_1}{M_{o2}K_2C_2} \times \frac{\frac{A_{w1}}{(1 - K_1A_{w1})(1 - K_1A_{w1} + C_1K_1A_{w1})}}{\frac{A_{w2}}{(1 - K_2A_{w2})(1 - K_2A_{w2} + C_2K_2A_{w2})}} \times \exp\frac{\mathcal{E}_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$
(17)

$$\frac{P_2}{P_1} = \frac{M_{o1}K_1C_1}{M_{o2}K_2C_2} \times \frac{A_{w1}(1 - K_2A_{w2})(1 - K_2A_{w2} + C_2K_2A_{w2})}{A_{w2}(1 - K_1A_{w1})(1 - K_1A_{w1} + C_1K_1A_{w1})} \times \exp\frac{\mathcal{E}_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$
(18)

$$0 = A_{w2} - \mathcal{N}(1 - K_2 A_{w2})(1 - K_2 A_{w2} + C_2 K_2 A_{w2})$$
(25)

$$0 = A_{w2} + (-\mathcal{N} + K_2 A_{w2} \mathcal{N})(1 - K_2 A_{w2} + C_2 K_2 A_{w2})$$
(26)

$$0 = A_{w2} - \mathcal{N} + K_2 A_{w2} \mathcal{N} - C_2 K_2 A_{w2} \mathcal{N} + K_2 A_{w2} \mathcal{N} - K_2^2 A_{w2}^2 \mathcal{N} + C_2 K_2^2 A_{w2}^2 \mathcal{N}$$
 (27)

$$0 = A_{w2} - \mathcal{N} + K_2 \mathcal{N} A_{w2} - C_2 K_2 \mathcal{N} A_{w2} + K_2 \mathcal{N} A_{w2} - K_2^2 \mathcal{N} A_{w2}^2 + C_2 K_2^2 \mathcal{N} A_{w2}^2$$
 (28)

$$0 = \underbrace{C_2 K_2^2 \mathcal{N} A_{w2}^2 - K_2^2 \mathcal{N} A_{w2}^2}_{} + \underbrace{K_2 \mathcal{N} A_{w2} + K_2 \mathcal{N} A_{w2} - C_2 K_2 \mathcal{N} A_{w2} + A_{w2}}_{} - \mathcal{N}$$
(29)

$$0 = (C_2 K_2^2 \mathcal{N} - K_2^2 \mathcal{N}) A_{w2}^2 + (2K_2 \mathcal{N} - C_2 K_2 \mathcal{N} + 1) A_{w2} - \mathcal{N}$$
(30)

$$0 = (-C_2K_2^2 + K_2^2)A_{w2}^2 + (-2K_2 + C_2K_2 - 1/\mathcal{N})A_{w2} + 1$$
(31)

$$A_{w2} = \frac{-(C_2K_2 - 2K_2 - 1/\mathcal{N}) \pm \sqrt{(C_2K_2 - 2K_2 - 1/\mathcal{N})^2 - 4(K_2^2(1 - C_2)) \times 1}}{2(K_2^2(1 - C_2))}$$
(34)

on which to base the Isoperm and investigate the effect this would have on changes in permanence induced by temperature and RH change. If it makes little or no difference regardless of how we calculate the Isoperm - then the point becomes merely academic, but if the difference is substantial then it will become a priority to substantiate the work of Zou et al.

The recalculation of the isoperm concept requires detailed knowledge of two equations: the Arrhenius equation for modeling deterioration rate, and the Guggenheim-Anderson-deBoer (GAB) equation so moisture content can be translated into the relative humidity for specifying HVAC control.

The Arrhenius equation's applicability to rate studies is well discussed^{8,1}. The most appropriate relation for describing moisture sorption for paper⁶ and quite possibly other structural organic macromolecules is the GAB equation. The GAB has a strong basis in physical modelling and thermodynamic relationships to the point the GAB equation can be derived in thermodynamic terms as shown by Monleon et al.¹³.

The materials for which conservation has the most data to resolve actual rates for the redefined isoperm equation are cellulosic paper (studies by CCI, PapriCan), and cellulose acetate film (studies by IPI). To properly use the proposed equation, both ageing and sorption isotherm studies on closely matched materials over a wide range of tempera-

ture and moisture content are required. This further limits the current pool of information.

The value of the isoperm concept is to make rational decisions on the long term storage environment of artifacts to minimize hydrolytic deterioration of key macromolecules. It can aid cost/benefit decisions by equating changes in humidity control to resultant lifetime extension especially if serious capital investment and energy consumption is being proposed. Based on the current isoperm model's predictions, it also provides a means to quantify the effects of proposed shifts from energy intensive climate control to more passive means for achieving energy conservation goals and this is particularly appropriate as sustainability of museum climate control becomes an ever more pressing issue as energy costs inevitably continue to rise. Lastly, as excessive heat is eschewed as an agent of deterioration, the isoperm is also tied to quantifying the effects of short term exposures such as heat and moisture used in treatment for re-shaping objects, and elevated temperature exposure (55 °C) for insect extermination.

Because the isoperm has a central point to make in preventive conservation, it was important to redefine the isoperm model in terms of testable properties and come to a full understanding of the underlying assumptions, with the eventual goal of demonstrating its application through experimental results.

Unfortunately, we have been unable to find satisfactory GAB parameters for paper or any other material which is relevant to museum application. We have therefore initiated experimental work with a TGA Q5000 SA sorption analyzer. This machine generates GAB parameters directly over the temperature range of interest. Once we have a consistent set of data we plan to publish a follow-up paper with the revised Isoperms.

4 References

- 1. X. Zou, T. Uesaka and N. Gurnagul, *Prediction of paper permanence by accelerated aging I, Kinetic analysis of the aging of Cellulose*, Cellulose, 1996, **3**, 243–267.
- 2. D. K. Sebera, *Isoperms. An environmental management tool*, http://cool-palimpsest.stanford.edu/byauth/sebera/isoperm/index.html (accessed 20. June 2009)
- 3. http://www.imagepermanenceinstitute.org/shtml_sub/dl_prescalc.asp (accessed 20. June 2009)
- 4. D. W. Grattan, *Isoperms recalculated*, verbal presentation at Canadian Association of Conservation (CAC-ACCR) Annual Conference, St. John's Newfoundland, May 18-20, 2007.
- 5. J. Chirife, H. A. Iglesias, *Equations for fitting water sorption isotherms of foods: Part 1 —- a review*, J. Food Technology, 1978, **13**, 159-174.

- 6. M. E. Parker, J. E. Bronlund, A. J. Mawson, *Moisture sorption isotherms for paper and paperboard in food chain conditions*, Packaging technology and science, 2006, **19**, 193 209.
- 7. J. R. Hulett, *Deviations from the Arrhenius equation*, Quarterly Reviews.1964. **18.** 227-242.
- 8. K. Connors, Chemical kinetics, Wiley-VCH, New York, 1990.
- 9. X. Zou, T. Uesaka, N. Gurnagul, *Prediction of paper permanence* by accelerated aging II, Comparison of the predictions with natural aging results, Celluolose, 1996, **3**, 269–279.
- 10. N. J. Bunce, C. L. Forber, C. McInnes, J. M. Hutson, *Single-step methods for calculating activation parameters from raw kinetic data*, J. Chem. Soc. Perkin Trans. II, 1988, 363 368.
- 11. S. Gál, *Ueber die ausdrucksweisen der konzentration des wasserdampfes bei asserdampfsorptionsmessungen*, Helvetica Chimica Acta, 1972, **55**, 1752-1757.
- 12. C. van den Berg, S. Bruin, *Water activity and its estimation in food systems: Theoretical aspects*, in: B. Rockland and G. F. Stewart (Eds), *Water activity: Influences on food quality*, Academic Press, New York, 1981.
- 13. M. Monleón Pradas, M. Salmerón Sànchez, G. Gallego Ferrer, J.L. Gómez Ribelles, *Thermodynamics and statistical mechanics of multilayer adsorption*, The Journal of Chemical Physics, 2004, **121**, 8524—8531