7.5 – Swimming Pool and Spa Chemical Safe Storage and Shipping Temperatures

Most chemical substances are subject to some decomposition at elevated temperatures, including some swimming pool and spa chemicals such as sanitizers and oxidizing agents. Department of Transportation (DOT) regulations governing the preparation of hazardous materials for transportation are described in the Hazardous Materials Transportation Act. Under these regulations, the offering for transportation of a material that is liable to decompose or polymerize at a temperature of 130°F (54.4°C) or less with evolution of a dangerous quantity of heat or gas is forbidden. The determination of whether a material is forbidden may be made by the Self Accelerating Decomposition Temperature (SADT) test. Accelerating rate calorimetry (ARC) and computer simulation offer an alternative to SADT testing and are discussed in this article.

Self Accelerating Decomposition Temperature (SADT)

SADT Test Procedure – The SADT test is carried out by placing the largest commercial package in an oven maintained at a constant temperature for 7 days. The minimum number of tests is two. If the sample survives at the lower temperature, fails at the higher temperature, and if the difference in the test temperature is not greater than 5.5°C, the SADT is then reported as an average of these two temperatures.

Journal of the Swimming Pool and Spa Industry
Volume 5, Number 2, pages 20–24

Accelerating Rate Calorimetry (ARC)

Procedure – In ARC, a sample (1–10 g) is placed in a metal bomb (e.g., Ti, volume ~10 mL) enclosed in a chamber maintained under adiabatic conditions. The bomb is heated step–wise (typically 5°C increments) followed by a 5–minute waiting period during which the calorimeter searches for evidence of self–heating by the sample. The calorimeter assumes an exotherm has started when the self–heat rate is ≥ 0.02°C/min. Once an exotherm has started, heat from the sample decomposition raises the temperature of the bomb and the sample while the calorimeter inputs only sufficient heat to offset losses to the outside air. The numerical data provided by the ARC consist of time, temperature, self–heat rate, and pressure. Plots of temperature vs time, self–heat rate vs temperature, time to maximum rate vs temperature, pressure vs temperature, and pressure rate vs temperature can be generated. The data provided allow calculation of heat of decomposition, rate constant, activation energy, and critical temperature (or temperature of no return).

Thermokinetic Theory – The temperature dependence of reaction rate can be described by a modified form of the Arrhenius equation (Townsend and Tou 1980):

1. $k = AT^2 \exp(-\Delta E/RT)$

where: k = rate constant, A = pre–exponential factor, T = °K, ΔE = activation energy, and R = gas constant (8.314J $\text{mol}^{-1}\ \text{K}^{-1}$). Assuming zero order (or initial rate kinetics), the energy balance for an adiabatic system is given by:

2. $MC_p dT/dt = \Delta HAT^2 \exp(-\Delta E/RT)$

where: M = mass, C_p = heat capacity, t = time, and ΔH = heat of reaction. Rearrangement gives the following differential equation for the initial rate of change of temperature with time due to self–heating:

3. $dT/dt = [\Delta H/(MC_p)]AT^2 \exp(-\Delta E/RT)$

Activation Energy – Taking Logs of both sides of equation 3 and rearranging gives:

4. $\text{Log}_e\,(dT/dt) = -\Delta E/RT + \text{Log}_e\,\{[\Delta H/(MC_p)]AT^2\}$

This is in the form: y = mx + b. Plotting Log_e (dT/dt) against 1/T shows an increasing self heat rate with increasing temperature which reaches a maximum and then falls off precipitously as the decomposing material is exhausted. An illustrative plot is shown in Figure 1. The activation energy ΔE is obtained from the slope (–ΔE/R), which is determined by drawing a tangent at the beginning of the self–heat plot. Using temperatures of 104°C (377.15K) and 170°C (443.15), which correspond to self–heat rates of 0.01 and 6.0°C/min, yields a value of 32,188 cal/mol as shown below.

5. $\Delta E = [\text{Log}_e\,(r_2/r_1)]R/(1/T_1 - 1/T_2)$

$\Delta E = [\text{Log}_e\,(6.0/0.01)]1.987/(1/443.15 - 1/377.15)$

$= 32{,}188$ cal/min.

The activation energy is also obtained from the temperature dependence of the rate constant and during critical temperature estimation (see

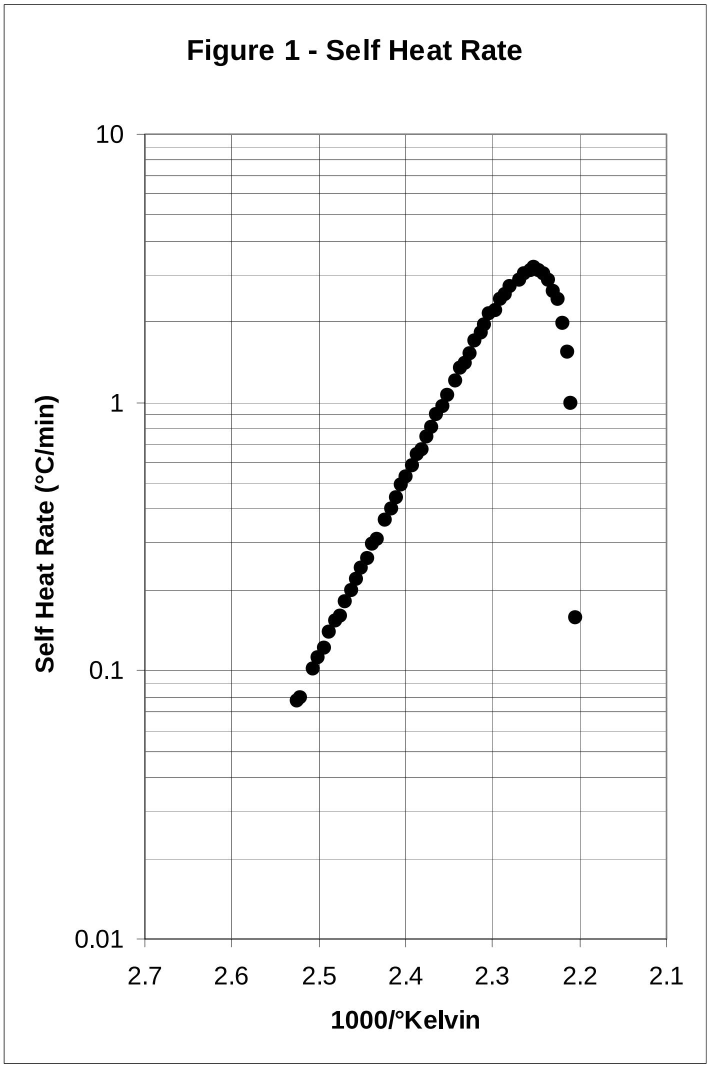

Figure 1 - Self Heat Rate

discussion below).

Rate Constant – The rate constant k (and activation energy) can be determined from the ARC data via the following equation:

6. $k = (dT/dt)/(T_f - T_t)\ \mathrm{min}^{-1}$

where: dT/dt = self heat rate (°C/min), T_f = final temperature (°C), and T_t is the temperature (°C) at time t (min) below maximum rate. A plot of $\log_e k$ vs 1/T °K gives the activation energy (from the slope = $\Delta E/R$) and the pre–exponential (factor from the y intercept).

Heat of Decomposition – The heat of decomposition (ΔH) is calculated from the ARC provided adiabatic temperature rise and the ϕ (phi) factor, which allows allocation of the heat effect entirely to the sample. The phi factor for the ARC run of Figure 1 is calculated using the following equation where: M_B (82.0g), M_S (2.5g), C_{PB} (0.11cal g^{-1} K^{-1}) and C_{VS} (0.5cal g^{-1} K^{-1}) are the masses and heat capacities of the bomb and sample, respectively.

7. $\phi = 1 + M_B C_{PB}/(M_S C_{VS}) = 1 + 82\bullet 0.11/(2.5\bullet 0.5)$
$= 8.22$

The value of ΔH is obtained from the adiabatic temperature rise T_{ab}.

8. $\Delta H = DT_{ab}\phi C_V$
$= (T_f - T_i)\ \phi C_V$
$= (180.3 - 122.7)\bullet 8.22\bullet 0.5$
$= 236.7$ cal/g

where: T_i and T_f are the initial and final temperatures, respectively.

Time to Maximum Rate – Integration of equation 3 and application of boundary conditions, gives the following equation for time to maximum rate (t_{mr}), also referred to as time to explosion.

9. $t_{mr} \cong RT^2/(\Delta E\, dT/dt) \cong RT^2 C_p M/(k\Delta H\Delta E)$

Material/Equipment Time Constant – Under steady–state conditions, thermal equilibrium is represented by the following heat–transfer equation:

10. $US(T - T_a) = M\Delta HAT^2\exp(-\Delta E/RT)$

where: U = thermal conductivity, S = container surface area, T is the product temperature, and T_a = ambient temperature. By varying T_a, it can be shown that there exists a unique temperature (the critical temperature T_c) above which thermal equilibrium cannot exist and thermal runaway occurs.

At the critical temperature (or temperature of no return), the adiabatic time to maximum rate $t_c = \tau$ (or time constant) is independent of decomposition – being a function of engineering parameters only. The time constant is calculable from the following equation:

11. $\tau = MC_p/(US)$

Critical Temperature Estimate –Taking Logs of both sides of equation 9 and rearranging gives:

12. $1/T = (R/\Delta E)\mathrm{Log}_e t_{mr} - (R/\Delta E)\mathrm{Log}_e(RC_pMT^2/\Delta E\Delta H)$

This is in the form: $y = mx + bT^2$. Values of t_{mr} are calculated using zero order self heat rates (SHR_0) adjusted for the phi factor. Zero order self–heat rates are calculated using the equation of the tangent line drawn in Figure 1. The equation of the tangent line is:

13. $\mathrm{Log}_e\ SHR_0 = -16.199(1/T) + 38.345$

Zero order self–heat rates adjusted for the phi factor are given by the following equation:

14. $SHR_{0(\phi)} = \exp(-16.199(1/T) + 38.345)\phi$

A Log–Log plot of 1/T vs t_{mr} should give a

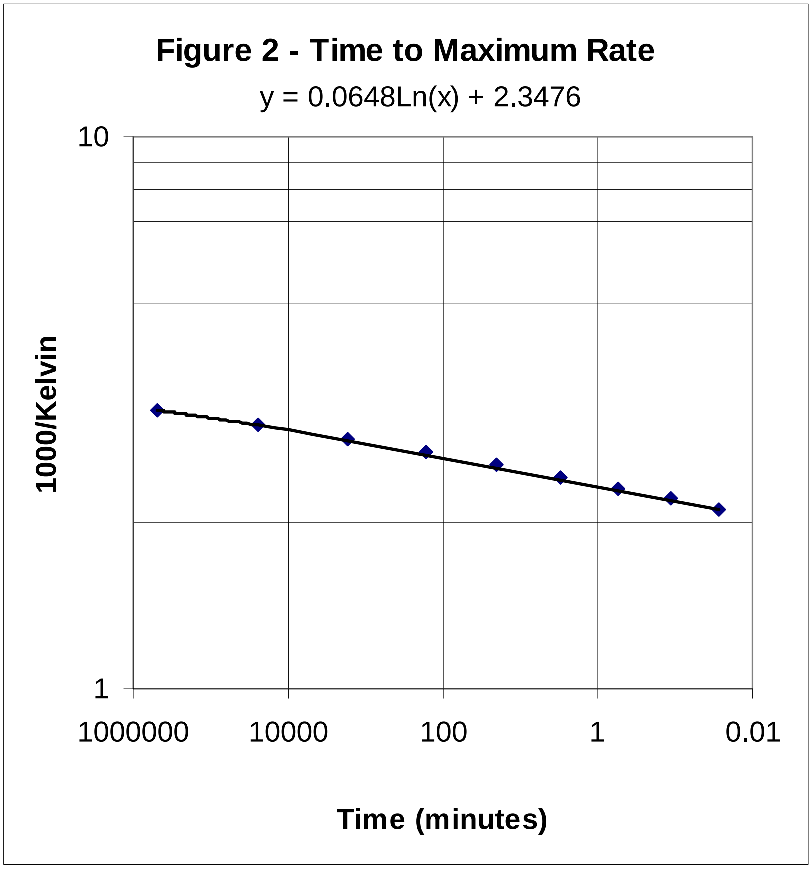

Figure 2 - Time to Maximum Rate

straight line with slope R/ΔE (see Figure 2). Linear regression can be employed to obtain an equation of the line and allow extrapolation to lower temperatures. The temperature at which the value of t_{mr} equals the time constant t is equal to the critical temperature (T_c).

Calculation of SADT from ARC – An equation for calculating T_{SADT} can be derived from ARC data (Fischer and Goetz 1991). Heat generation (Q_G) is given by:

15. $Q_G = A\exp(-\Delta E/RT)M\Delta H$

Heat loss (Q_L) is given by:

16. $Q_L = US(T - T_0)$

where: T_0 = ambient air temperature. Equating Q_G and Q_L gives:

17. $A\exp(-\Delta E/RT)M\Delta H = US(T - T_0)$

Differentiation yields:

18. $\Delta E/RT^2 A\exp(-\Delta E/RT)M\Delta H = US$

Setting $T = T_C$, and substituting from equation 17.

19. $\Delta E/RT_C^2 US(T_C - T_0) = US$

Cancellation and rearrangement gives:

20. $T_0 = T_C - RT_C^2/\Delta E$

where: $T_0 = T_{SADT} + 273.15$, $T_C = T_{NR} + 273.15$

T_{NR} (@ τ) $= MC_P/US$

Determination of Critical Temperature via Computer Simulation

The diffusion of heat in a cylindrical container of material with internal heat generation can be described by the following second order partial differential equation (Rohsenow and

Hartnett 1973):

21. $(1/\alpha)\partial T/\partial t = (1/r)\partial T/\partial r + \partial^2T/\partial r^2 + \partial^2T/\partial x^2 + Q/K$

where:

∂ = partial differential operator
T = temperature
t = time
r = radial distance
x = axial distance
$\alpha = K/(\rho C_p)$ = thermal diffusivity
K = thermal conductivity
ρ = bulk density
C_p = heat capacity
Q = rate of heat generation

The independent variable T in equation 21 is related to independent variable time (t) and spatial coordinates (x and r) in the conducting media by means of a heat balance differential equation derived from Fourier's law of heat conduction $Q_n = -K\partial T/\partial n$; where: Q_n is a vector and n is a direction normal to the surface A.

Although equation 21 cannot be solved analytically, it can be solved using the methods of finite differences. The temperature is determined at only a finite number of discrete points called nodes. A nodal network in a cylindrical container can be obtained by subdividing the radial and axial distances in a vertical mid–plane into small segments. Due to symmetry, only a single mid–plane in a hemi–cylinder need be considered. Because the temperature of a particular node at some time is independent of the temperatures at other nodes at the same time, the temperature of that node (with vertical and horizontal coordinates i, j) at time (n + 1) can be calculated explicitly in terms of its temperature and that of its neighboring nodes at time (n).

The partial derivatives in equation 21 are replaced with finite difference approximations obtained from a Taylor's series expansion of the temperatures in the control volume to yield a system of algebraic equations.

An alternate approach is to use the Fourier Heat Theorem:

22. $dq/dt = KAdT/dx$

where: dq/dt is the instantaneous rate of heat flow through cross sectional area A subject to a temperature gradient equal to dT/dx. The differential equation 22 can be approximated using finite increments (Δ) in place of infinitesimal differentials (d) as follows:

23. $\Delta q = Q = KA\Delta T\Delta t/\Delta x$

Equation 23 can be applied to a generalized nodal cell. The vertical and horizontal heat flows in and out of the cell and the heat accumulated allow calculation of the temperature changes with time.

A computer program can be written to perform the calculations as a function of time. The input to the computer program includes the physical and chemical data and constants listed above as well as the container dimensions. The heat generating term requires not only the heat of reaction but also the kinetics, which can be determined by differential thermal analysis (DTA) and differential scanning calorimetry (DSC). For example, the kinetic constants can be determined according to ASTM E698–79 (1984).

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