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Estimating Rates of Spreading and Evaporation of Volatile Liquids

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Follow these guidelines to calculate how fast a pool of spilled liquid will spread across a surface, evaporate and potentially form a flammable mixture with the air.

Despite operators' meticulous efforts to avoid spills during the handling of volatile liquids, accidents can, and do happen. In such cases, the ability to predict the rate at which the liquid spreads and how fast it evaporates prove invaluable. The former would be instrumental in planning and designing containment. The latter would be useful in finding the vapor concentration of the substance in ambient air, which would help one to determine the electrical area classification, fraction of lower explosive limit achieved, and address other similar safety-related issues. In this article, methodologies will be presented for calculating spill spreading and evaporation rates. Examples featuring these methods are used to find the liquid mass remaining at any given moment and the time required to evaporate the entire spill.

First, one must assume that: the volume of spilled liquid is known (*e.g.*, derived from batch data as the largest volume used in a process) or can be derived (*e.g.*, using the flowrate from a leak point and approximate duration of the leak); the liquid is well characterized in terms of density (ρ), surface tension (σ), viscosity (μ) and vapor pressure (P_{vp}); the liquid is at ambient temperature and barometric pressure, which are known; and the spill progresses as a liquid spreading across a smooth, level surface.

How far will a spill spread?

A liquid that is spilled on a flat surface will progress in three regimes *(1)*:
• the gravity-inertia regime, in which gravity tends to spread the fluid and is opposed by the inertia of the fluid
• the gravity-viscous regime, in which gravity tends to spread the fluid and is opposed by the viscosity of the fluid
• the viscous-surface tension regime, in which the liquid viscosity is opposed by the surface tension of the fluid.

Most volatile liquids have viscosities less than or close to that of water (~1 cP), and will enter the viscous-surface tension regime in a few seconds. Eq. 1 yields the time required to enter the viscous-surface tension regime:

$$t_{vs} = 0.023462(gV\rho\mu/\sigma) \tag{1}$$

where g is the gravitational constant (ft/s^2), V is the spill volume (ft^3), and ρ (lb/ft^3), μ (cP) and σ (dyne/cm) are evaluated at the ambient temperature (T_A) or the temperature of the air above the liquid pool. With t_{vs} one can calculate the radius of the spill at zero time (a_0) (*i.e.*, at the onset of evaporation):

$$a_0 = 1.413142(\sigma V t_{vs}/\mu)^{1/4} \qquad (2)$$

What is the shape of the spill?

The shape of the volume of spilled liquid should be modeled in such a way as to enable the calculation of the area exposed to the atmosphere. In the real world, the spill assumes the shape of a spherical cap. If one determines the proportions of the spherical cap (and those of the corresponding hypothetical sphere), one can find the exposed surface area of the spill. The volume of a spherical cap is calculated as *(2)*:

$$V_{cap} = (\pi h/6)(3a^2 + h^2) \qquad (3)$$

$$V_{cap} = (\pi h^2/3)(3r_{sph} - h) \qquad (4)$$

where h is the depth of liquid at the center of the spill, a is the radius of the spill, and r_{sph} is the radius of the hypothetical sphere of which the cap is part. The initial radius of the spill (*i.e.*, the radius measured immediately following the brief interval t_{vs} after the liquid is first spilled) is noted as a_0. It is calculated with Eq. 2, where the volume of the spherical cap is V_0, and the time with respect to the evaporation process is zero. Note that during the spreading phase, no evaporation takes place.

Correspondingly, the height of the spherical cap at the center, h_0, the maximum depth of the spill, is calculated as:

$$h_0^3 + 3a^2h_0 - (6V_0/\pi) = 0 \qquad (5)$$

This cubic equation can be solved analytically, or, more
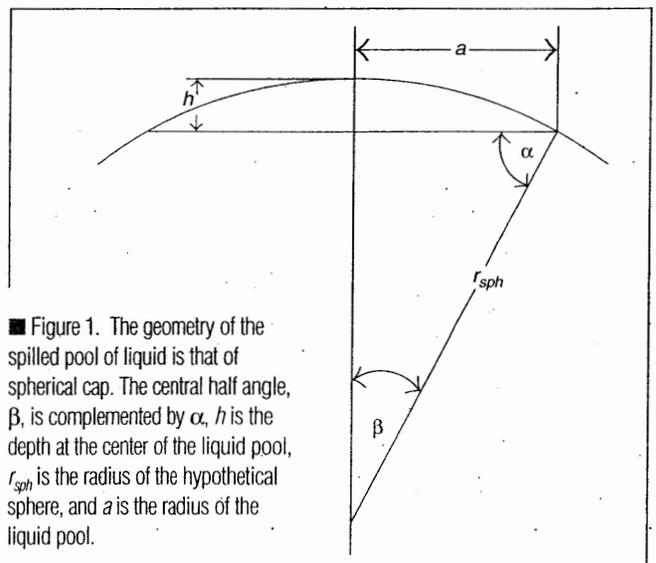
■ Figure 1. The geometry of the spilled pool of liquid is that of spherical cap. The central half angle, β, is complemented by α, h is the depth at the center of the liquid pool, r_{sph} is the radius of the hypothetical sphere, and a is the radius of the liquid pool.

conveniently, by the use of a spreadsheet solver function. If one assumes that the central half angle (β) of the cap (Figure 1) remains constant during the course of the spill, then:

$$\sin\beta = a_0/r_0 \tag{6}$$

where r_0 is the initial radius of the spherical cap, and:

$$\tan\beta = h_0/a_0 \tag{7}$$

Then, substituting Eq. 7 into Eq. 5:

$$a_0^3\tan^3\beta + 3a_0^3\tan\beta - (6V_0/\pi) = 0 \tag{8}$$

A collection of terms leads to the expression:

$$\tan^3\beta + 3\tan\beta - (1/a_0^3)(6V_0/\pi) = 0 \tag{9}$$

Eq. 9 is a cubic equation and may be solved for $\tan\beta$ using a spreadsheet. Readers seeking a rigorous solution should consult Ref. 3 and use the key words, "cubic equation."

With $\tan\beta$ (and therefore β), h and a in hand, one can calculate the surface area of the cap using *(3)*:

$$A_{cap} = 2\pi r_{sph}h \tag{10}$$

Weisstein defines r_{sph} as *(2)*:

$$r_{sph}\sin\alpha = r - h \tag{11}$$

where α is the complement of β:

$$\alpha = \pi/2 - \beta \tag{12}$$

Other important relationships include:

$$r_{sph}\sin\beta = a \tag{13}$$

$$a\csc\beta = r_{sph} \tag{14}$$

$$h = a\tan\beta \tag{15}$$

$$a = h\cot\beta \tag{16}$$

These equations will come in handy when seeking a solving equation for h. It is now possible to write the unsteady-state mass balance on the spill, assuming that the evaporative mass flux (E) — or the evaporation rate, normalized over the area exposed to the environment — remains constant:

$$-dW/dt = -\rho dV_{cap}/dt \tag{17}$$

$$-dW/dt = EA_{cap} \tag{18}$$

$$-dW/dt = E(2\pi r_{sph}h) \tag{19}$$

Here, A_{cap} and V_{cap} are the surface area (ft^2) and volume (ft^3) of the spherical cap at any time t (min); W is liquid mass (lb); ρ is liquid density (lb/ft^3); E is mass flux (lb/ft^2-min); and r_{sph} and h are measured in ft. It is assumed that β is constant throughout the course of the spill. Eq. 4 may be rearranged to solve for r_{sph}:

$$r_{sph} = (1/3)(3V_{cap}/\pi h^2 + h) \tag{20}$$

Since $V_{cap} = W/\rho$ $\tag{21}$

by substitution:

$$r_{sph} = (1/3)(3W/\pi\rho h^2 + h) \tag{22}$$

Substitution of Eq. 16 in Eq. 5 to define h yields:

$$h^3 + 3(h^2\cot^2\beta)h - 6V/\pi = 0 \tag{23}$$

$$h^3 + 3h^3\cot^2\beta - (6V/\pi) = 0 \tag{24}$$

Eq. 24 may be rewritten as:

$$h^3(1 + 3\cot^2\beta) = 6V/\pi \tag{25}$$

Taking the cubic root of both sides yields the following:

$$h = (6V/(\pi(1 + 3\cot^2\beta)))^{1/3} \tag{26}$$

$$h = (6W/(\pi\rho(1 + 3\cot^2\beta)))^{1/3} \tag{27}$$

$$h = bW^{1/3} \tag{28}$$

where:

$$b = (6W/(\pi\rho(1 + 3\cot^2\beta)))^{1/3} \tag{29}$$

Combining Eqs. 22 and 27, and performing extensive rearrangement and substitution leads to:

$$r_{sph} = (W^{1/3}/3)[(3(1 + 3\cot^2\beta)^2/4\pi\rho)^{1/3} + (6/\pi\rho(1 + 3\cot^2\beta))^{1/3}] \tag{30}$$

$$r_{sph} = cW^{1/3} \tag{31}$$

where:

$$c = 3(1 + 3\cot^2\beta)^2/4\pi\rho)^{1/3} + (6/\pi\rho(1 + 3\cot^2\beta))^{1/3} \tag{32}$$

The constants b and c are expressed in units of ft/lb$^{1/3}$ when English units are used. Subsequently, an expression for A_{cap} in terms of the mass of the liquid may be derived:

$$A_{cap} = 2\pi r_{sph}h \tag{33}$$

$$A_{cap} = 2\pi bc W^{2/3} \tag{34}$$

Eq. 34 is substituted into Eq. 18 to yield:

$$-dW/dt = E(2\pi bc W^{2/3}) \tag{35}$$

Rearranging Eq. 35 yields:

$$W^{-2/3}dW/dt = -(2\pi bc)E \tag{36}$$

Integration results in:

$$3W_1^{1/3} - 3W_2^{1/3} = 2\pi bcE(t_2 - t_1) \tag{37}$$

where W_1 and W_2 are the mass in the spill at times t_1 and t_2, respectively:

$$W_2 = (W_1^{1/3} - 2\pi bcE(t_2 - t_1)/3)^3 \tag{38}$$

If one assumes that β and E are constant, the cubic root of the mass in the spherical cap decreases linearly with time.

Determining the evaporative flux

There are three methods for estimating E. Two apply to a spill exposed to a moving air stream. The third method, Stiver-MacKay, can be extended to cover the case of a spill exposed to still air.

1. U.S. Air Force method. This empirical method is based on the evaporation of hydrazine at ambient temperatures (4). The evaporative flux for other liquids is estimated using the following equation, which is normalized for the effects of temperature and the properties of a liquid other than hydrazine:

$$E = 4.66 \times 10^{-6} u^{0.75} T_F M(P_{vp,S}/P_{vp,H}) \tag{39}$$

In the equation above, M is molecular weight (lb/lbmol), $P_{vp,S}$ and $P_{vp,H}$ are vapor pressures of the spilled substance and hydrazine respectively (torr) and T_F is a temperature correction factor defined conditionally as follows:

$$\text{When } T_P < 32°F, \ T_F = 1 \tag{40}$$

$$\text{When } T_P > 32°F, \ T_F = 1 + 0.00133(T_P - 32)^2 \tag{41}$$

In the original work, $P_{vp,S}$ and $P_{vp,H}$ are expressed in torr, but when using Eqs. 41 and 42, any consistent set of units is applicable, since the vapor pressure contribution is dimensionless. The original work also evaluates the vapor pressures at T_A. Although T_A is not equal to T_P, it is reasonable to assume they are equivalent, barring special situations (*e.g.*, a cold liquid spilled in a warm environment).

2. U.S. EPA method. Below is a slightly modified form of the empirical equation developed by the U.S. Environmental Protection Agency (EPA) to define evaporative flux (5, 6):

$$E = 0.28u^{0.78}M^{0.667}P_{vp,S}/RT_A \tag{42}$$

where u is the air velocity (ft/min) and $P_{vp,S}$ is expressed in units of torr, since the vapor-pressure contribution term is not dimensionless.

3. Method of Stiver-MacKay. This method employs a mass transfer coefficient explicitly. As such, it lends itself to situations other than that of a liquid pool exposed to a moving air stream (7, 8, 9, 10):

$$E = kP_{vp,S}M/R'T_{RA} \tag{43}$$

In this case, k is the mass transfer coefficient measured in ft/min or ft/s, and R' is the ideal gas constant measured in ft³torr/lbmol°R. One can define k using the following empirical relationships:

$$k = 0.00293u \text{ (ft/s)} \tag{44}$$

$$k = 0.1758u \text{ (ft/min)} \tag{45}$$

Beyond constant flux — forced convection

The derivations presented thus far are predicated on the assumption that the evaporative flux is independent of the geometry (and thus the characteristic dimension) of the spill. However, the mass-transfer coefficient — and therefore flux — is usually a function of some characteristic length of the geometry in question. E will vary with the changing geometry of the spill because, in the real world, there is usually movement of air above the spilled liquid. This creates a pressure differential, causing evaporative mass transfer to occur by forced convection. To account for the effects of forced convection, a mass-transfer coefficient that depends upon a characteristic dimension of the spill is introduced into the evaporative flux equation.

It is assumed here that the term "flow," except for the transient case of the spreading of the spilled liquid, refers to the air above the spill. Typically, the radius of curvature of the spill is sufficiently large such that the flow of air behaves like air flowing past a flat plate. This flow can be turbulent or laminar.

Bennett and Myers state that for flow past a flat plate, the laminar-to-turbulent transition occurs at about $Re \approx 3 \times 10^5$ (11), where Re is the Reynolds number calculated for a plate of length L as:

$$Re_L = u\rho L/\mu \tag{46}$$

L is a characteristic length of the geometry in question, and u, ρ and μ are the velocity, density and viscosity of the moving fluid, respectively. L takes the form of $2a$, where a is the radius of the spherical cap. The velocity is assumed to have been measured (*e.g.*, by a local

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anemometer) or determined otherwise (*e.g.*, by a local weather report). The ρ and μ of air are obtained from tables of physical properties in a standard reference (*e.g.*, *Perry's Chemical Engineers' Handbook*).

Bennett and Myers show a dimensionless expression for the mass transfer coefficient for laminar flow using the Sherwood (*Sh*), Schmidt (*Sc*) numbers:

$$Sh = 0.66Re_L^{1/2}Sc^{1/3} \tag{47}$$

$$Sc = v/D_{AB} \tag{48}$$

$$Sc = \mu/\rho D_{AB} \tag{49}$$

$$Sh = kL/D_{AB} \tag{50}$$

where μ is liquid viscosity (lb/ft-min) and D_{AB} is the diffusivity of substance A diffusing through substance B (ft^2/min) and may be found by the methods described by Reid, *et al.* (*12*). Equating Eqs. 47 and 50, and solving for k:

$$k = 0.66(D_{AB}/L)Re_L^{1/2}Sc^{1/3} \tag{51}$$

$$k = 0.66(D_{AB}/L)(Lu\rho/\mu)^{1/2}(\mu/\rho D_{AB})^{1/3} \tag{52}$$

$$k = 0.66(D_{AB}/L^{1/2})(u\rho/\mu)^{1/2}(\mu/\rho D_{AB})^{1/3} = \tag{53}$$

$$k = (2a)^{-1/2}(0.66D_{AB}^{2/3}u^{1/2}(\rho/\mu)^{1/6}) \tag{54}$$

The characteristic dimension a can be expressed in terms of the mass of the spherical cap using a combination of Eqs. 16 and 28:

$$a = b\cot\beta W^{1/3} \tag{55}$$

Thus,

$$k = W^{-1/6}(2b\cot\beta)^{-1/2}D_{AB}^{2/3}u^{1/2}(\rho/\mu)^{1/6} \tag{56}$$

$$k = vW^{-1/6} \tag{57}$$

Solving for v yields:

$$v = D_{AB}^{2/3}(u/2b\cot\beta)^{1/2}(\rho/\mu)^{1/6} \tag{58}$$

The result of substituting Eq. 57 in the Stiver-MacKay relationship for flux yields:

$$E = vP_{vp,S}M/R'T_A W^{-1/6} \tag{59}$$

Use of Eq. 59 in the unsteady-state mass balance, followed by integration, results in this empirical equation for forced-convection evaporative mass flux in the laminar flow regime:

$$W_1^{1/2} - W_2^{1/2} = j(t_2 - t_1), \tag{60}$$

where:

$$j = 2\pi bcvP_{vp,S}M/R'T_{RA} \tag{61}$$

Thus, for laminar flow, when accounting for a change in the mass transfer coefficient (and therefore E) as a function of the changing dimensions of the liquid pool, the square root of W decreases linearly with time.

In many standard texts (*11*), the analogy between heat and mass transfer developed originally by Chilton and Colburn is used to derive mass-transfer relationships for known geometries and flow conditions based on dimensionless-numbers for heat transfer.

As a corollary, if one has a relation for heat transfer for a given geometry (*e.g.*, flow past a flat plate), then by analogy, one has a relation for mass transfer for that same geometry. For turbulent flow, this analogy between heat and mass transfer is used to find E. For heat transfer involving turbulent flow past a flat plate, Bennett and Myers give this correlation for the Nusselt number (*13*):

$$Nu = 0.0365Re^{4/5}Pr^{1/2} \tag{62}$$

The exponent on the Prandtl number (*Pr*) is open to some debate. Based on other work (*14*), an exponent of 1/2 is used here. Thus, the mass-transfer analog is assumed to be:

$$Sh = 0.0365Re^{4/5}Sc^{1/2} \tag{63}$$

Eq. 63 is equated with Eq. 50 to solve for k. As for laminar flow, subsequent expressions for k are derived and substituted into the solving equation for E in the Stiver-MacKay relationship. The integration of the unsteady-state mass balance yields the following equation for turbulent convection:

$$W_2 = (W_1^{2/5} - 2q(t_2 - t_1)/5)^{5/2} \tag{64}$$

where q and x are constants, defined as:

$$q = 2\pi bcxP_{vp,S}M/R'T_A \tag{65}$$

$$x = 0.0365D_{AB}^{1/2}u^{4/3}(\rho/\mu)^{1/10}(2b\cot\beta)^{-1/3} \tag{66}$$

In the equations defining q and x, constants b and c are calculated as per Eqs. 29 and 32, respectively.

Extending the method to free convection

Next, the evaporative flux is examined under the conditions of free convection. The air above the pool is assumed to be completely still, and the driving force for mass transfer is the difference in concentration of the volatile compound between the liquid pool and the air above the pool.

To adapt the method explained for forced convection to the case of free convection, one needs a free-convection mass-transfer coefficient, which is again derived using the Chilton and Colburn analogy between heat and mass transfer, as applied to free convection past a flat plate of liquid.

For free convection in the laminar flow regime (*i.e.*, when $10^5 \leq Gr_L Pr \leq 2 \times 10^7$, where Gr is the dimensionless Grashof number for laminar flow), the heat transfer coefficient may be expressed as:

$$Nu = 0.54(Gr_L Pr)^{1/4} \tag{67}$$

and, for free convection in the turbulent flow regime: (*i.e.*, when $2 \times 10^7 \leq Gr_L Pr < 3 \times 10^{10}$):

$$Nu = 0.14(Gr_L Pr)^{1/3} \tag{68}$$

Using the Chilton and Colburn analogy, the mass transfer coefficient for free convection in the laminar flow regime: (*i.e.*, when $10^5 \leq Gr_{AB} Sc \leq 2 \times 10^7$) is:

$$Sh = 0.54(Gr_{AB} Sc)^{1/4} \tag{69}$$

and, for free convection in the turbulent flow regime (*i.e.*, when $2 \times 10^7 \leq Gr_{AB} Sc < 3 \times 10^{10}$) is:

$$Sh = 0.14(Gr_{AB} Sc)^{1/3} \tag{70}$$

In the equations above, Gr and Sc are defined as *(15)*:

$$Gr_{AB} = L^3 \rho g \Delta\rho_A/\mu^2 \tag{71}$$

$$Sc = \mu/\rho D_{AB} \tag{72}$$

For the purposes of this article, $L = 2a$. In addition, $\Delta\delta$ refers to the difference in concentration of the evaporating species between the boundary layer of liquid and the bulk fluid above it. Usually, the concentration of the evaporating species in the bulk fluid is zero or effectively zero.

Following a procedure similar to that used previously, one obtains for laminar flow:

$$W_2 = (W_1^{5/12} - (12z/5)(t_2 - t_1))^{12/5} \tag{73}$$

where:

$$z = 2\pi bcy P_{vp,S} M/R'T_A \tag{74}$$

$$y = 0.54((D_{AB})^3 g\Delta\delta/bc\cot\beta\mu)^{1/4} \tag{75}$$

Follow the procedure used for laminar flow to assess turbulent free convection:

$$W_2^{1/3} = (W_1^{1/3} - (n/3)(t_2 - t_1))^3 \tag{76}$$

where:

$$n = (2\pi bcm P_{vp,S} M/R'T_A) \tag{77}$$

and:

$$m = 0.14(D_{AB})^{2/3}(g\Delta\delta/\mu)^{1/3} \tag{78}$$

Rarely is the outdoor atmosphere completely still for any appreciable period of time. Therefore, for spills that occur under the condition of light winds to calm air, it is suggested that the estimated time for evaporation is calculated based on the average of the forced convection and free convection cases, since the actual situation lies somewhere between these two extremes. Furthermore, the upper limit on the product of the Gr and Sc numbers may limit the applicability of this analysis to small spills.

Example problems

Physical and transport properties, where required, are calculated from empirical correlations given by Yaws *(16)*.

Example 1. Assume 50 gal of methanol spills onto a level surface outdoors. A local thermometer reads $T_A = 59°F$, and a local anemometer gives an average wind speed of $u = 5$ mi/h. Estimate the greatest depth of the spill (h) and the time it will take the spill to evaporate ($t_2 - t_1$).

Summarize the known conditions and the physical properties of methanol: $P_{vp} = 69.058$ mmHg, $M = 32.044$ lb/lbmol, $W = 332.24$ lb, $R = 555$ mmHg-ft³/lbmol°R, $\mu = 0.619$ cP, $\sigma = 24.869$ dyne/cm, $\rho = 49.707$ lb/ft³, and $D_{AB} = $ lb/ft.

As a first pass, assume that the evaporative flux is independent of the dimensions of the spill (*i.e.*, E remains constant during the evaporation process). A preview of the calculations reveals that the EPA method yields the shortest evaporation time, while the Stiver-MacKay method yields the longest evaporation time. Therefore, for a conservative estimate, the Stiver-MacKay method will be used.

Calculate the initial spreading time, t_{vs}, using Eq. 1:

$t_{vs} = 0.023462[(32.174$ ft/s²$)(50$ gal $\times 7.48$ gal/ft³$)$ $(49.707$ lb/ft³$)(0.619$ lb/ft-s$)/24.869$ dyne/cm$] = 6.24$ s.

Calculate the pool radius at t_{vs} using Eq. 23:

$a_0 = 1.413142$ $[(24.869$ dyne/cm$)(6.684$ ft³$)(6.243$ s$)/$ $(0.619$ cP$)]^{1/4} = 9.04$ ft.

In this calculation, the unit conversion factors for μ and σ have been worked into the coefficient. The liquid pool is assumed to take the form of a spherical cap, due to the effects of surface tension. Given the volume and the radius at time zero, solve Eq. 5 for the maximum depth of the pool at its center:

$h^3 + 3(9.04$ ft$)^2 h = 6V_0/\pi = 6(50$ gal$/(7.48$ gal/ft³$))/\pi = $

12.77 ft³; therefore, $h = 0.052$ ft

β is found by rearranging Eq. 9 and using a spreadsheet solver function:

$\tan^3\beta + 3\tan\beta = (1/a_0^3)(6V_0/\pi)$. Thus, $\tan\beta = 0.005755$ rad, and $\beta = 0.00576$.

Per Eqs. 43 and 45:

$E = 0.1758(5 \text{ mi/h})(69.058 \text{ mmHg})(32.044 \text{ lb/lbmol}) / ((555 \text{ mmHg-ft}^3/\text{lbmol°R})(59 + 453.49°R)) = 6.76 \times 10^{-3}$ lb/ft²min.

Use this result in Eq. 37 to find the evaporation time, $t_2 - t_1$. Solve for t_2 with $t_1 = 0$ and $W_2 = 0$. This leads to:

$$t_2 = 3W_1^{1/3}/2\pi bcE$$

where:

$b = (6W/(\pi\rho(1 + 3\cot^2\beta)))^{1/3} = 7.51 \times 10^{-3}$ ft/lb$^{1/3}$

and

$c = (3(1 + 3\cot^2\beta)^2/4\pi\rho)^{1/3} + (6/(\pi\rho(1 + 3\cot^2\beta)))^{1/3} = 113.42$ ft/lb$^{1/3}$.

Thus:

$t_2 = 3(332.24 \text{ lb})^{1/3} / (2 \times 3.14 \times (7.51 \times 10^{-3} \text{ ft/lb}^{1/3}) \times (113.42 \text{ ft/lb}^{1/3})(6.76 \times 10^{-3} \text{ lb/ft}^2\text{min})) = 574.17$ min.

Example 2. Repeat Example 1, but this time, assume that the evaporative flux is a function of the pool radius (a_0) under conditions of forced convection. Since the flux varies throughout the evaporation process., one needs an integrated mass balance that accounts for the effect of the pool's shrinkage on the flux. The Stiver-MacKay method is the only one that includes an explicit term for k, and will be used to perform the calculations. All of the physical properties and constants (*e.g.*, b and c) are consistent with those cited in Example 1.

First, determine whether convection is turbulent or laminar using Eq. 46:

$Re = (5 \text{ mi/h})(5,280 \text{ ft/mi})(0.076 \text{ lb/ft}^3)(2 \times 9.04 \text{ ft}) / ((0.018 \text{ cP})(2.419 \text{ lb/ft-h})/\text{cP}) = 8.33 \times 10^5$.

Since Re is greater than 3×10^5, flow is turbulent and Eq. 64 should be used. This equation requires the determination of several constants. D_{AB} is determined using physical property estimation methods described in Ref. 12, 11-4.4

Time (t), min	Mass of Spill (W_2), lb	Volume of Spill (V), ft³	Radius of Spill (a), ft
0	6.64	1.337E-01	1.28
1	6.34	1.275E-01	1.26
2	6.04	1.215E-01	1.24
4	5.47	1.100E-01	1.20
6	4.94	9.930E-02	1.16
8	4.44	8.931E-02	1.12
10	3.98	8.002E-02	1.08
12	3.55	7.139E-02	1.04
14	3.15	6.340E-02	1.00
16	2.79	5.604E-02	0.96
18	2.45	4.927E-02	0.92
20	2.14	4.306E-02	0.88
22	1.86	3.740E-02	0.84
24	1.60	3.226E-02	0.80
26	1.37	2.762E-02	0.76
28	1.17	2.344E-02	0.72
30	0.98	1.971E-02	0.68
35	0.60	1.215E-02	0.57
40	0.34	6.827E-03	0.47
45	0.17	3.342E-03	0.37
50	0.06	1.306E-03	0.27
55	0.02	3.300E-04	0.17
60	0.00	2.415E-05	0.07

Table. Spill mass and volume vs. time under conditions of turbulent free convection.
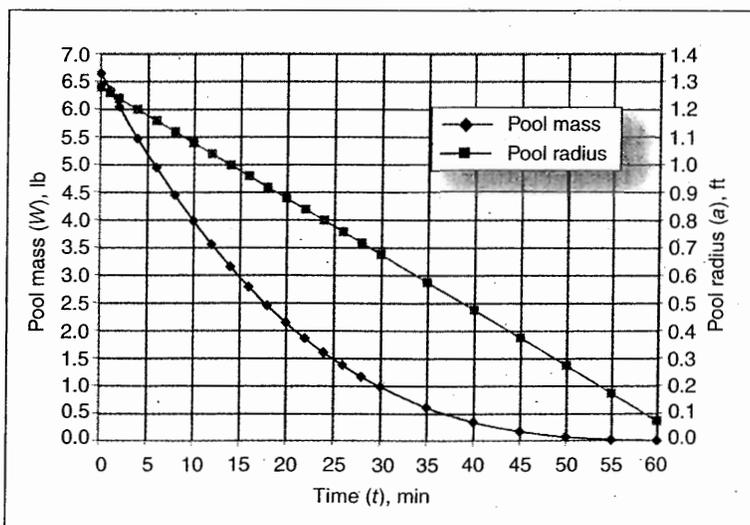
Figure 2. Pool radius and liquid mass remaining as a function of time for the case of free convection in the turbulent flow regime.

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and Table 11-1 to be 0.160 cm^2/s = 0.010 ft^2/min. The central half-angle is calculated as $\beta = 0.00576$ rad. Also, per Eq. 66:

$x = 0.0365((0.010$ ft^2/min$)^{1/2})((5$ mi/h $\times 88$ ft/min/(mi/h)$)^{4/3}(0.619$ cP$(0.04032$ lb/ft min/cP)$)^{1/10}(2(7.51 \times 10^{-3}$ ft/lb$^{1/3})$cot$(0.00576$ rad$))^{-1/3} = 11.62$ ft-lb$^{1/15}$/min.

And, per Eq. 65:

$q = 2\pi bcxP_{vp,S}M/R'T_A = 2\pi(7.51 \times 10^{-3}$ ft/lb$^{1/3}) \times (113.42$ ft/lb$^{1/3})(11.62$ ft-lb$^{1/15}$/min$)(69.058$ mmHg$) \times (32.0422$ lb/lbmol$)/((555$ mmHg-ft^3/lbmol°R$)(59 + 453.49$°R$)) = 0.484$ lb$^{2/5}$/min.

Assume $W_2 = 0$ and $t_1 = 0$, and solve for t_2 using Eq. 64, which is rearranged as:

$t_2 = 5W_1^{2/5}/2q = 5 \times (332.24$ lb$)^{2/5}/(2 \times 0.484) = 52.68$ min.

As may be expected, the predicted time required to evaporate the entire spill decreases significantly when one accounts for a change in the evaporative flux with the decreasing size of the pool.

Example 3. Consider a smaller spill ($V_0 = 5$ gal) of methanol. Once again, assume that the evaporative flux varies during the evaporation process. Assume that $u = 0$ ft/s and thus, only free convection takes place. Also, assume that the air above the spill contains a negligible concentration of vapor. Calculate the amount of time it will take to evaporate the entire spill.

The Stiver-MacKay method will be used because it includes an explicit term for k. This case exhibits turbulent flow free convection, since $ScGr = \sim 3.9 \times 10^9$. Thus, Eq. 76 is used with $W_2 = 0$ and $t_1 = 0$ to calculate t_2:

$t_2 = 3W_1^{1/3}/n$

where:

$n = 2\pi bcmP_{vp,S}M/R'T_A = 0.0887$ (lb/min)$^{1/3}$

$m = 0.14(D_{AB})^{2/3}(g\Delta\delta/\mu)^{1/3} = 7.93$ ft/min.

Thus, $t_2 = 63.6$ min.

Example 4. Building on Example 3, in which the evaporative flux varies, calculate the mass of liquid remaining, along with the volume and radius of the spill, as evaporation progresses, until all of the liquid is evaporated.

Use Eq. 76 to solve for W_2 with $t_1 = 0$ and t_2 varying from 1 min to 60 min. To solve for a, find V using W_2/ρ. Then, using Eq. 2, solve for a. The results are shown in the Table and Figure 2. **CEP**