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THE NON-STEADY OUTFLOW OF PROPANE VAPOR FROM A RAILROAD TANK CAR

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16. Abstract

This report discusses the venting of vapors from rail tank cars. Two particular problem areas are addressed, namely the non-steady character of the flow in the final blow-down stage and the influence of real gas effects on flow predictions. Equations are developed with which the non-steady mass flow rate, the stagnation temperature and pressure drop and the mass left in the tank as a function of time can be predicted for vapor flow out of a finite-sized tank. The influence on the predicted flow rates due to the use of different equations of state (e.g. perfect gas equation, van der Waal's equation, Starling's equation) is shown and discussed. Example calculations are carried out for propane. The developed equations and calculation methods are valid for most other vapors and gases of industrial fluids commonly shipped in rail tank cars.

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Preface

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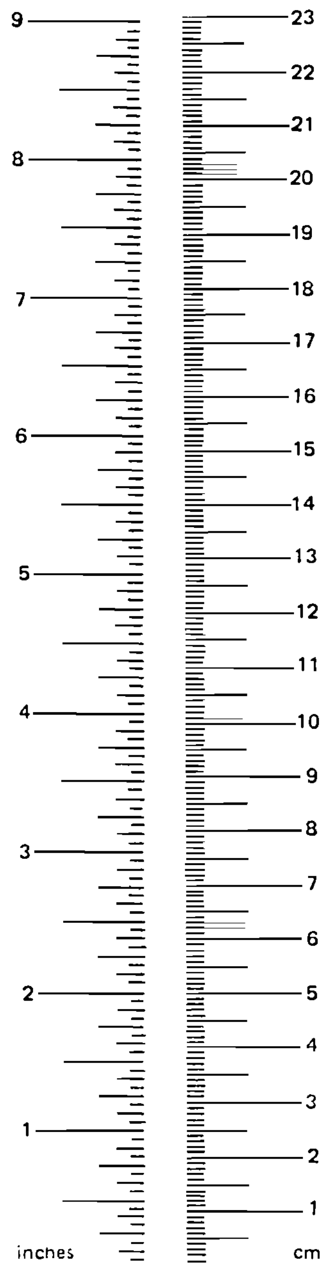
METRIC CONVERSION FACTORS

Approximate Conversions to Metric Measures

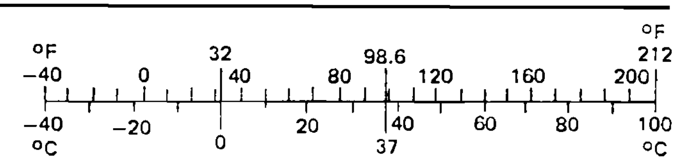
Symbol	When You Know	Multiply by	To Find	Symbol
		LENGTH		
in	inches	*2.5	centimeters	cm
ft	feet	30	centimeters	cm
yd	yards	0.9	meters	m
mi	miles	1.6	kilometers	km
		AREA		
in^2	square inches	6.5	square centimeters	cm^2
ft^2	square feet	0.09	square meters	m^2
yd^2	square yards	0.8	square meters	m^2
mi^2	square miles	2.6	square kilometers	km^2
	acres	0.4	hectares	ha
		MASS (weight)		
oz	ounces	28	grams	g
lb	pounds	0.45	kilograms	kg
	short tons (2000 lb)	0.9	tonnes	t
		VOLUME		
tsp	teaspoons	5	milliliters	ml
Tbsp	tablespoons	15	milliliters	ml
fl oz	fluid ounces	30	milliliters	ml
c	cups	0.24	liters	l
pt	pints	0.47	liters	l
qt	quarts	0.95	liters	l
gal	gallons	3.8	liters	l
ft^3	cubic feet	0.03	cubic meters	m^3
yd^3	cubic yards	0.76	cubic meters	m^3
		TEMPERATURE (exact)		
°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C

*1 in. = 2.54 cm (exactly). For other exact conversions and more detail tables see NBS Misc. Publ. 286. Units of Weight and Measures. Price $2.25 SD Catalog No. C13 10 286.



Approximate Conversions from Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
		LENGTH		
mm	millimeters	0.04	inches	in
cm	centimeters	0.4	inches	in
m	meters	3.3	feet	ft
m	meters	1.1	yards	yd
km	kilometers	0.6	miles	mi
		AREA		
cm^2	square centimeters	0.16	square inches	in^2
m^2	square meters	1.2	square yards	yd^2
km^2	square kilometers	0.4	square miles	mi^2
ha	hectares (10,000 m^2)	2.5	acres	
		MASS (weight)		
g	grams	0.035	ounces	oz
kg	kilograms	2.2	pounds	lb
t	tonnes (1000 kg)	1.1	short tons	
		VOLUME		
ml	milliliters	0.03	fluid ounces	fl oz
l	liters	2.1	pints	pt
l	liters	1.06	quarts	qt
l	liters	0.26	gallons	gal
m^3	cubic meters	36	cubic feet	ft^3
m^3	cubic meters	1.3	cubic yards	yd^3
		TEMPERATURE (exact)		
°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature	°F



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NOMENCLATURE

A	area (cross sectional flow area)
c	sonic velocity
c_p	specific heat at constant pressure
c_v	specific heat at constant volume
CS	control surface
CV	control volume
g	local gravitational constant
g_c	$\left(32.174 \frac{lb_m\ ft}{lb_f\ s^2} = 1 \frac{kg\ m}{N\ s^2}\right)$
h	specific enthalpy
J	mechanical-thermal energy equivalent $\left(778.26 \frac{ft \cdot lb_f}{Btu} = 1 \frac{Nm}{J}\right)$
k	specific heat ratio: $k = \frac{c_p}{c_v}$
K_1, K_3	as defined in text (Equations 24 and 26)
$\dot{m}$	mass flow rate
M	mass
p	pressure
$\dot{Q}$	rate of total heat input
R	gas constant (ratio of universal gas constant to molecular weight of gas; $R_{propane} = 0.18855 \frac{kJ}{kgK} = 35.04 \frac{ft\ lb_f}{lbm\ R}$)
s	specific entropy
t	time

t_c	time duration from start of blow down to the instant at which choked flow ceases
T	temperature
u	specific internal energy
v	specific volume
$\mathcal{V}$	total volume
V	total velocity
Z	compressibility factor
ρ	density
asterisk*	refers to quantities at critical section when choked flow exists
asterisk^o	refers to properties in the ideal gas state
subscript$_o$	refers to isentropic stagnation conditions
subscript$_{oi}$	refers to initial stagnation conditions
subscript$_{atm}$	refers to atmospheric (ambient) conditions

I. Introduction

The pressure relief capability of safety valves is under investigation at the University of Maryland under sponsorship of the Department of Transportation. The completed study will provide industry and the Department of Transportation with accurate valve sizing equations, mass flow charts and tables for propane, propylene, n-butane, ethylene, anhydrous ammonia, butadiene, chlorine, vinyl chloride and several other commodities generally shipped in rail tank cars.

This report discusses the flow of gases and vapors from a rail tank car (or any other pressure vessel) to the atmosphere during the final phase of the venting process, when only vapor is left in the tank. Two major points are addressed, namely, the non-steady flow due to a finite pressure reservoir, and the effect on the blow-down process if the vapor is not assumed to be a perfect or ideal gas (if a more complex equation of state is selected to describe the thermodynamic behavior of the vapor).

The analytical non-steady flow equations given in Chapter III are valid for any vapors or gases which exhibit perfect gas behavior. For more complex equations of state an analytical solution to the blow-down process does not exist in closed form and the problem must be solved numerically, as is shown in Chapter IV. The question of how predicted mass flow rates will differ for vapor flow when, instead of the perfect gas equation, more realistic and complex equations of state are applied, is shown in Chapter V. The particular example chosen is the flow of propane vapor from a DOT 112 type rail tank car, starting at the instant at which there is no more liquid propane in the tank. The vapor was assumed to flow through a safety valve which has a critical area of 7.86 square inches and a valve coefficient for vapor flow of 0.88; the valve was assumed to stay fully open during the entire flow period. The initial pressure in the tank car was 300 psia and the initial temperature

$170^{\circ}F$. The various equations of state which are compared to each other in this example are: the perfect gas equation with different compressibility factors (1.000, 0.700 and 0.7567), the ideal gas equation (specific heat ratios are not constant), Van der Waal's equation, the Benedict-Webb-Rubin equation and Starling's equation.

II. Steady Flow Equations for Perfect Gases

The energy equation for a system with a control volume CV and a control surface CS is

$$\dot{Q} - \sum \dot{W} = \frac{\partial}{\partial t}\iiint_{CV} \left(u + \frac{V^2}{2} + gz\right)\rho dV + \iint_{CS} \left(u + pv + \frac{V^2}{2} + gz\right)\rho \bar{V}\cdot d\bar{A} \quad (1)$$

where the work rate term $\dot{W}$ includes shaft work, shear work and all other work. Assuming steady state during the flow process and negligible heat transfer and work input, equation (1) reduces to

$$\iint_{CS} \left(u + pv + \frac{V^2}{2} + gz\right) \rho \bar{V}\cdot d\bar{A} = 0. \quad (2)$$

For uniform flow, equation (2) can be rewritten as

$$\left(h_2 + \frac{V_2^{\,2}}{2} + gz_2\right) \rho_2 V_2 A_2 - \left(h_1 + \frac{V_1^{\,2}}{2} + gz_1\right) \rho_1 V_1 A_1 = 0, \quad (3)$$

and the continuity equation (steady state) becomes

$$\dot{m} = \rho_1 V_1 A_1 = \rho_2 V_2 A_2 = \rho V A \quad (4).$$

For gas flow the changes in potential energy due to change in elevation are negligible and equations (3) and (4) yield the general, steady state velocity equation

$$V = \sqrt{2 J g_c \left(h_o - h\right)} \tag{5}$$

The constants J and g_c which must be introduced when the customary engineering units are used have the following values:

$$J = 778.26 \frac{ft\ lb_f}{Btu} = 1 \frac{Nm}{J}$$

and

$$g_c = 32.174 \frac{lb_m\ ft}{lb_f\ s^2} = 1 \frac{kg\ N}{m\ s^2}$$

Equation (5) is the basic equation for the velocity of the flowing medium which is brought from the stagnation state (velocity equals zero) given by the stagnation enthalpy h_o to the velocity V at which point the corresponding enthalpy has the value h.

In order to derive expressions for the mass flow rate of a medium flowing from a given upstream state to a given downstream state, the equation of state of the flowing medium must be known or prescribed and the thermodynamic flow process must be known or prescribed. This report discusses the flow of gases. The equation of state assumed in this chapter is the equation of state for an ideal gas,

$$pv = RT. \tag{6}$$

Furthermore, assuming the gas to be calorically perfect, i.e., the specific heats are constant,

$$\left(h_o - h\right) = c_p \left(T_o - T\right) , \tag{7}$$

$$R = \left(c_p - c_v\right) J \tag{8}$$

and

$$k = \frac{c_p}{c_v} \tag{9}$$

Equation (5) becomes

$$V = \sqrt{2 g_c \left(\frac{k}{k-1}\right) R\, T_o \left(1 - \frac{T}{T_o}\right)} \tag{10}$$

In order to relate the properties of the stagnation state to the properties at any flow condition the thermodynamic process which governs the flow must be prescribed. In the flow of gases, viscous losses due to shear play a minor role in short flow sections, i.e. the loss in stagnation pressure due to friction is very small. In the absence of shock waves or major flow restrictions the isentropic flow assumption is valid, so that

$$\frac{T}{T_o} = \left(\frac{p}{p_o}\right)^{\frac{k-1}{k}} \tag{11}$$

and

$$\frac{\rho}{\rho_o} = \left(\frac{p}{p_o}\right)^{\frac{1}{k}} \tag{12}$$

With the isentropic relationship given by equation (11), equation (10) can be rewritten

$$V = \sqrt{\left(\frac{2k}{k-1}\right) g_c \; R \; T_o \left[1 - \left(\frac{p}{p_o}\right)^{\frac{k-1}{k}}\right]} \qquad (13).$$

The mass flow rate $\dot{m}$ can now be derived from the continuity equation (equation (14)), and equation (13) using the ideal gas equation (6) and the isentropic relationship given by equation (12). The mass flow rate is

$$\dot{m} = A \frac{p_o}{\sqrt{\frac{ZR}{g_c} T_o}} \sqrt{\frac{2k}{k-1}\left[\left(\frac{p}{p_o}\right)^{\frac{2}{k}} - \left(\frac{p}{p_o}\right)^{\frac{k+1}{k}}\right]} \qquad (14)$$

where the compressibility factor Z was introduced to account for real gas effects according to the relation

$$pv = ZRT \qquad (15).$$

Equation (14) gives the mass flow rate of a gas from a reservoir (e.g. a pressure vessel) in which the temperature and pressure are T_o and p_o respectively. The pressure p in equation (15) is the static pressure at that downstream section at which the cross sectional area is A. Suppose the flow problem to be analyzed is that of a pressure vessel from which a gas flows to the atmosphere through a converging nozzle. The static pressure at different sections of the nozzle will decrease in the flow direction. At the nozzle exit a free jet will form. In the flow example discussed here, the static pressure is then the atmospheric pressure and the area A is the nozzle exit area.

Equation (14) shows that for a given stagnation temperature T_o and stagnation pressure p_o the mass flow rate will increase with decreasing downstream pressure. This is, however, only possible as long as the flow velocity at the nozzle throat is less than sonic. Once sonic flow exists at the throat of the nozzle a decrease in receiver pressure will no longer influence the mass flow rate. The nozzle is said to be choked; for choked flow to exist, the pressure in the reservoir must be

$$p_o \geq \frac{p^*}{\left(\frac{2}{k+1}\right)^{\frac{k}{k-1}}} \qquad (16).$$

From the isentropic relationships (11) and (12) it follows that

$$\frac{T^*}{T_o} = \frac{2}{k+1} \qquad (17)$$

and

$$\frac{\rho^*}{\rho_o} = \left(\frac{2}{k+1}\right)^{\frac{1}{k-1}} \qquad (18).$$

The mass flow rate equation for choked flow follows directly from equation (14) and expression (16) where the equality sign is used in the latter expression; the mass flow rate is

$$\dot{m} = A^* \frac{p_o}{\sqrt{\frac{ZR}{g_c} T_o}} \sqrt{k \left(\frac{2}{k+1}\right)^{\frac{k+1}{k-1}}} \qquad (19).$$

Equation (19) is the mass flow rate equation for choked gas flow; it can be used in predicting venting rates from pressure vessels as long as 1, the condition given by equation (16) is satisfied; 2, the gas behaves like a perfect gas; 3, no heat transfer takes place; 4, the vessel is so large that during the time in which the flow is considered, the stagnation temperature T_o, and the stagnation pressure p_o stay constant; and 5, the flow losses are negligible. Choked flow will exist as long as expression (16) is satisfied. For choked flow from a pressure vessel to the atmosphere through holes, valves or converging nozzles the atmospheric pressure can be substituted for p^* in (16).

III. Non-Steady Flow Equations for Perfect Gases

In most blow-down flow processes from pressure vessels the pressure in the vessel is sufficiently high so that choked flow exists during most of the blow-down period. The governing mass flow equation is therefore equation (19). However, pressure vessels are finite in size, i.e. the pressure in the vessel will drop as a function of time and consequently the mass flow rate is also a function of time. In this chapter the non-steady mass flow equation will be derived.

Let the volume of the vessel be denoted by V , then the mass inside the vessel at any instant is

$$M(t) = V\rho_o(t) \qquad (20).$$

Taking the derivative with respect to time yields

$$\dot{m}(t) = -V\frac{d\rho_o}{dt} \qquad (21)$$

since the volume V is constant. The minus sign was included because mass outflow is considered, i.e. the stagnation density decreases with time. Writing equation (21) in the form

$$\dot{m}dt = - V\, d\rho_o \tag{22}$$

and introducing equations (19), (15), (11) and (12) yields

$$\int_{t=0}^{t=t} \frac{A^*}{V} K_1 \sqrt{\frac{g_c\ ZR\ T_{oi}}{\rho_{oi}^{\ k-1}}}\, dt = - \int_{\rho_{oi}}^{\rho_o} \rho_o^{\ -\frac{k+1}{2}}\, d\rho_o \tag{23}$$

where

$$K_1 = \sqrt{k \left\{\frac{2}{k+1}\right\}^{\frac{k+1}{k-1}}} \tag{24}.$$

Integration of equation (23) yields

$$\frac{\rho_o\ (t)}{\rho_{oi}} = \left[\left(\frac{A^*\ K_3 \sqrt{T_{oi}}}{V}\right) t + 1\right]^{\frac{2}{1-k}} \tag{25}$$

where

$$K_3 = \frac{k-1}{2} \sqrt{g_c\ ZR\ k \left(\frac{2}{k+1}\right)^{\frac{k+1}{k-1}}} \tag{26}.$$

The subscripts oi refer to the stagnation condition at t = 0 i.e. the stagnation condition before the flow started.

Writing the isentropic relationships in the form

$$\frac{p_o(t)}{p_{oi}} = \left(\frac{\rho_o(t)}{\rho_{oi}}\right)^k \tag{27}$$

and

$$\frac{T_o(t)}{T_{oi}} = \left(\frac{p_o(t)}{p_{oi}}\right)^{\frac{k-1}{k}} \tag{28}$$

the time-dependent mass flow rate for choked flow is obtained from equation (19) and (25). The result is

$$\dot{m}(t) = \frac{A^* p_{oi}}{\sqrt{\frac{ZR}{g_c} T_{oi}}} K_1 \left[F(t)\right]^{\frac{k+1}{k-1}} \tag{29}$$

where

$$F(t) = \frac{1}{\left[\left(\frac{A^* K_3 \sqrt{T_{oi}}}{V}\right) t + 1\right]} \tag{30}.$$

The time-dependent stagnation pressure, temperature and density in the tank follow directly from equations (25), (27) and (28);

$$p_o(t) = p_{oi}\left[F(t)\right]^{\frac{2k}{k-1}} \tag{31}$$

$$T_o (t) = T_{oi} \left[F (t) \right]^2 \qquad (32)$$

and

$$\rho_o (t) = \rho_{oi} \left[F (t) \right]^{\frac{2}{k-1}} \qquad (33).$$

The time t_c until choking stops during blow down to the atmosphere is derived from equation (31) and the relationship (16) where the equal sign is used and $p^* = p_{atm}$. The latter equality is true for converging choked nozzles. After some algebraic manipulation the result in the following form is obtained.

$$t_c = \frac{V}{A^* K_3 \sqrt{T_{oi}}} \left\{ \left[\left(\frac{2}{k+1}\right)^{\frac{k}{k-1}} \left(\frac{p_{oi}}{p_{atm}}\right) \right]^{\frac{k-1}{2k}} - 1 \right\} \qquad (34)$$

The mass M (t) which is in the tank at any time t can be derived by integrating equation (29) or by using equation (33). If the mass of the gas initially in the tank is denoted by M_i then

$$M (t) = M_i \left[F (t) \right]^{\frac{2}{k-1}} \qquad (35).$$

The non-steady mass flow rate during choked flow from a finite pressure reservoir to the atmosphere and the accompanying non-steady decreases in stagnation pressure, stagnation temperature and stagnation density are given by equations (29), (31), (32) and (33) respectively. It was assumed that the gas is a calorically and thermally perfect gas and that the gas undergoes only isentropic processes. When a more complex and generally more realistic equation of state is assumed rather than the perfect gas equation, a closed form analytical solution for the non-steady mass flow rate is not possible and the problem must be solved numerically.

IV. Numerical, Non-Steady Flow Calculations for Real Gases

The relationships developed in the previous two chapters are valid for any gas which behaves like a perfect gas. Unfortunately, for certain flow situations, such approximations are not valid, and more complex equations of state, such as the Van der Waal's or Starling's must be used. In general it is not possible to derive analytically equations in closed form for mass flow rates; hence numerical methods must be employed.

Consider a gas which satisfies the following equation of state;

$$p = p\ (\rho,\ T) \tag{36}$$

It is possible, using equation (36) and caloric information (such as ideal gas enthalpy), to derive expressions for other thermodynamic properties of interest in flow calculations (enthalpy, entropy and sonic velocity) as functions of density and temperature. Sallet and Palmer [1] have done this for Starling's equation of state; these relations and those for a Van der Waal's gas are given in the appendix.

Utilizing all previously stated assumptions about the flow situation, and replacing the perfect gas relations with those derived from equation (36) for the real gas, yields the following set of equations for the non-steady, choked flow problem;

mass flow rate:

$$\dot{m}\ (t) = \rho^{*}\ c\ (\rho^{*},\ T^{*})\ A^{*} \tag{37}$$

energy:

$$h\left(\rho_o, T_o\right) - h\left(\rho^*, T^*\right) - \frac{\left[c\left(\rho^*, T^*\right)\right]^2}{2J\, g_c} = 0 \qquad (38)$$

continuity:

$$\dot{m}(t) = -V \frac{d\rho_o}{dt} \qquad (39)$$

isentropic flow:

$$s\left(\rho^*, T^*\right) = s_{oi} = s\left(\rho_{oi}, T_{oi}\right) \qquad (40)$$

and isentropic expansion in vessel:

$$s_{oi} = s\left(\rho_o, T_o\right) \qquad (41)$$

where all densities and temperatures are evaluated at time t.

The condition for existence of choked flow, equation (16), becomes

$$p\left(\rho^*, T^*\right) \geq P_{atm} \, .$$

The flow equations may be solved numerically by the following procedure. The stagnation state of the gas in the vessel is assumed to be known at time t. The exit (starred) state is then found by solving equations (38) (energy) and (40) (isentropic flow) simultaneously for ρ^* and T^* at time t. From equation (37), the mass flow rate is calculated. Equation (39) (continuity equation), written in forward, finite difference form as

$$\rho_o\left(t + \Delta t\right) = \rho_o(t) - \dot{m}(t)\frac{\Delta t}{V} \, ,$$

is then used to give the density of the gas in the vessel at time $t + \Delta t$. The new vessel temperature, $T_0(t + \Delta t)$, is found by solving equation (41) (isentropic expansion). This procedure is repeated for each time step until the flow is no longer choked; i.e.

$$p(\rho^*, T^*) < p_{atm} \quad .$$

Convergence of the forward time differencing is checked by decreasing the time step, Δt, and comparing the time at which the choked flow condition is no longer satisfied.

V. Blow-Down of Propane Vapor from a Rail Tank Car

In order to simulate the blow-down of propane vapor from a rail tank car, the methods and equations developed in the previous two chapters were used. The tank car was treated as a simple vessel with the following properties;

Volume = 127.43 m^3 (4500 ft^3),

Critical Valve Area = 0.507 x 10^{-2} m^2 (7.86 in^2),

Valve Coefficient = 0.88 and hence

Effective Valve Area = 0.446 x 10^{-2} m^2 (6.92 in^2).

When the blow-down begins, the pressure of the propane in the tank car was assumed to be 2.068 MPa (300 psia) and its temperature 350° K (170° F).

Three sets of blow-down calculations were made assuming perfect gas behavior (with $k = 1.14$), each using a different compressibility factor, Z. The three values of Z used were 1.0, 0.7 and 0.7567. The last value was determined as the compressibility factor predicted by Starling's equation of state at the initial stagnation conditions.

Four sets of calculations were made with various approximations to the real gas behavior. The first assumed ideal gas behavior, but did not assume constant specific heats. The other three calculations were for Van der Waal's, Starling's and Benedict-Webb-Rubin (BWR) equation of state. The results for the BWR equation were virtually identical to those using Starling's equation, and hence, will not be presented. The coefficients for the BWR equation were taken from ref. 2, those for Van der Waal's from ref. 3, and the coefficients for Starling's equation (as well as expressions for h^o and s^o), were taken from ref. 4.

The results of the blow-down simulations are presented in Figures 1 through 3. Figure 1 gives the pressure in the pressure vessel (stagnation pressure) as a function of time when several different equations of state are used to describe the thremodynamic behavior of the propane vapor. Figure 2 compares the predicted mass flow rates at various times, after the start of venting when the different equations of state for propane vapor are used, while Figure 3 compares the mass of propane vapor which is predicted to be left in the vessel, again for various equations of state.

VI. Discussion

This article discusses the non-steady venting of gases and vapors from pressure vessels to the atmosphere. Two questions are addressed, namely how does the finite size of the pressure vessel influence the rate of pressure, temperature, density and mass flow decrease and how does the choice of equation of state influence these predicted results.

The first question was treated using a perfect gas undergoing isentropic expansion. The flow process was restricted to choked flow, as only choked flow is of interest when the venting of pressure vessels is discussed. The results are shown in equations (29) through (33). It is seen that the initial mass flow rate, the initial stagnation pressures, temperatures and densities must be multiplied with a time dependent function $\left[F\ (t)\right]^C$ where C is either a constant determined by the specific heat constants of the gas or a numerical constant. The function F (t) includes terms for the vessel volume V and the venting area A^*. In the non-steady flow example discussed in chapter V and shown in Figures 1 through 3, the calculations in which the propane vapor is expressed by a perfect gas equation can be performed either by using the numerical method indicated or by simply making use of the explicit solutions given in chapter III.

The second question is of importance because currently used methods in sizing pressure relief valves for vessels which contain liquified gases assume that the valve remains in the vapor space of the vessel and that the fluid which flows through the valve can be modeled as a perfect gas with a suitable compressibility factor. This investigation showed that this assumption is indeed valid and fully sufficient for the flow of propane vapor, under conditions normally encountered in the storage and transport of LPG provided that the compressibility factor is properly selected. Starling's equation of state is reputed to be the most accurate equation of state for propane in the literature to date. It is seen from Figures 1 and 3 that the vessel pressure and the mass of vapor left in the tank as predicted when using Starling's equation agree well with the non-steady pressure and mass predictions when the perfect gas equation with a compressibility factor of 0.7567 is employed. The use of the perfect gas equation, however, is much simpler as the explicit solutions developed in chapter III can be used and the use of the computer is not necessary. While calculations with the perfect gas equation with Z = 0.7567 slightly underestimates the stagnation pressures, the mass flow rates are somewhat overestimated as seen in Figure 2.

The compressibility factor of Z = 0.7567 was calculated from Starling's equation using the given initial stagnation conditions. It is of interest to see how the predicted non-steady pressure and mass flow rates differ when a compressibility factor is chosen which is given in standard thermodynamic texts such as reference 3. This is shown in Figures 1 to 3 by the curve denoted "Perfect Gas, Z = 0.7." Other thermodynamic equations of state which appeared to be of interest and which were used in the flow predictions shown in Figures 1 through 3 were the Benedict-Webb-Rubin equation (all results coincided with results based on Starling's equation), the Van der Waal's equation, the perfect gas equation with Z = 1.0 and the ideal gas equation.

VII. References

1. D.W. Sallet and M.E. Palmer, "The Calculation of the Thermodynamic Properties of Propane, Propylene, N-Butane and Ethylene," FRA-ORD 76/300, April 1980, 157 pages.
2. M. Benedict, G.W. Webb and L.C. Rubin, "An Empirical Equation for Thermodynamic Properties of Light Hydrocarbons and Their Mixtures," Journal of Chemical Physics, Vol. 8 (1940), pp. 334-345.
3. J.S. Hsieh, Principles of Thermodynamics, McGraw-Hill Book Co., New York, 1975, p. 89.
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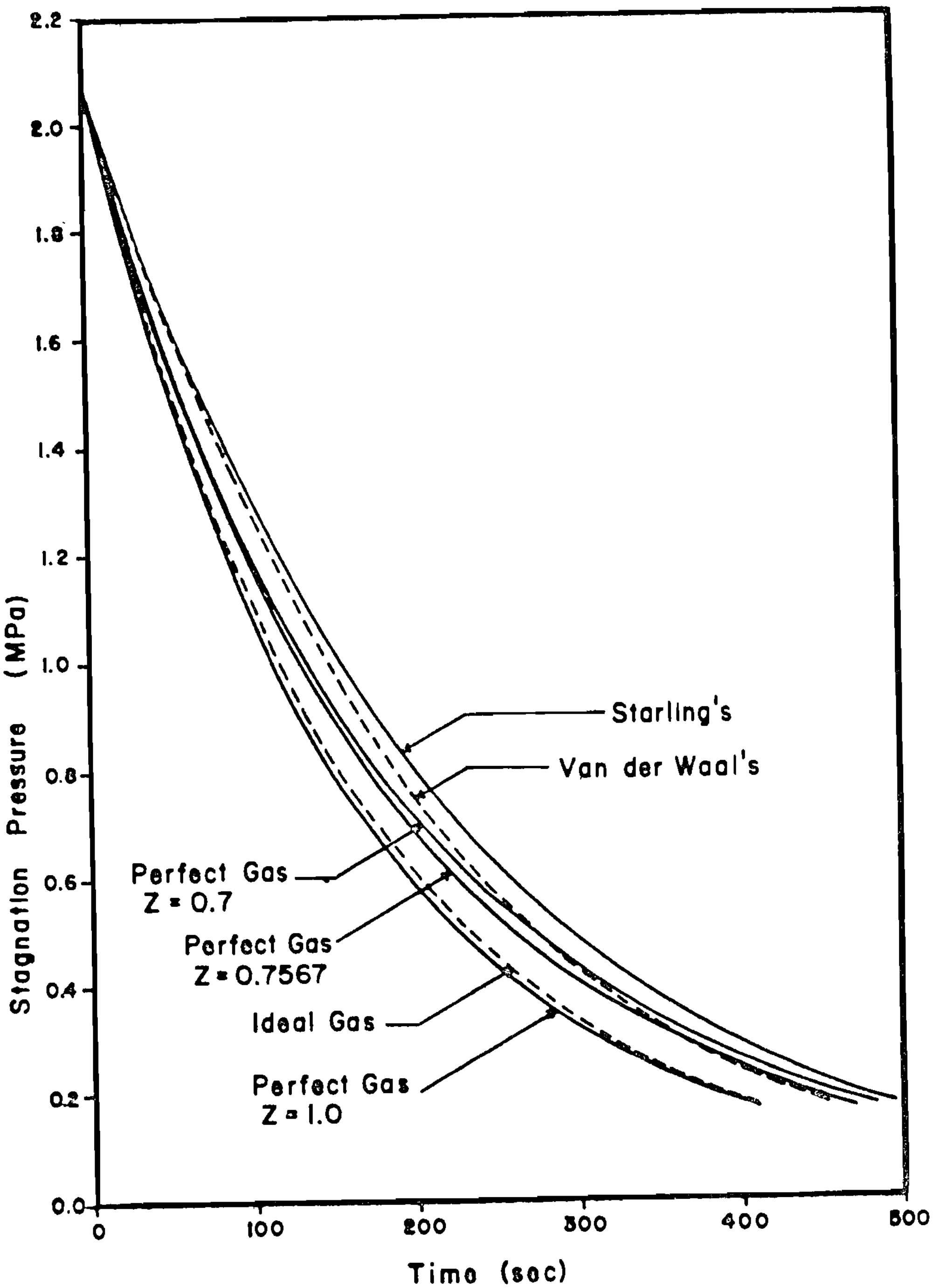

Figure 1: Stagnation pressure as a function of time as predicted using various equations of state for propane vapor.

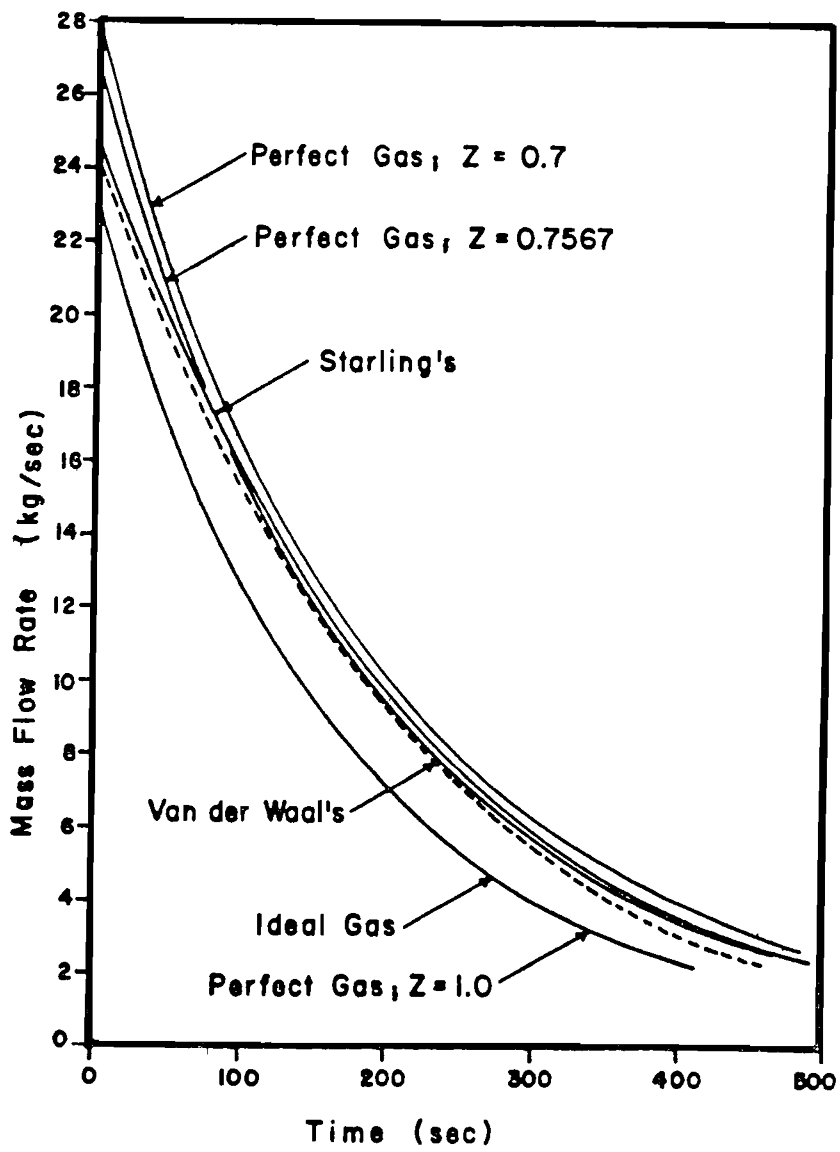

Figure 2: Mass flow rate as a function of time as predicted using various equations of state for propane vapor.

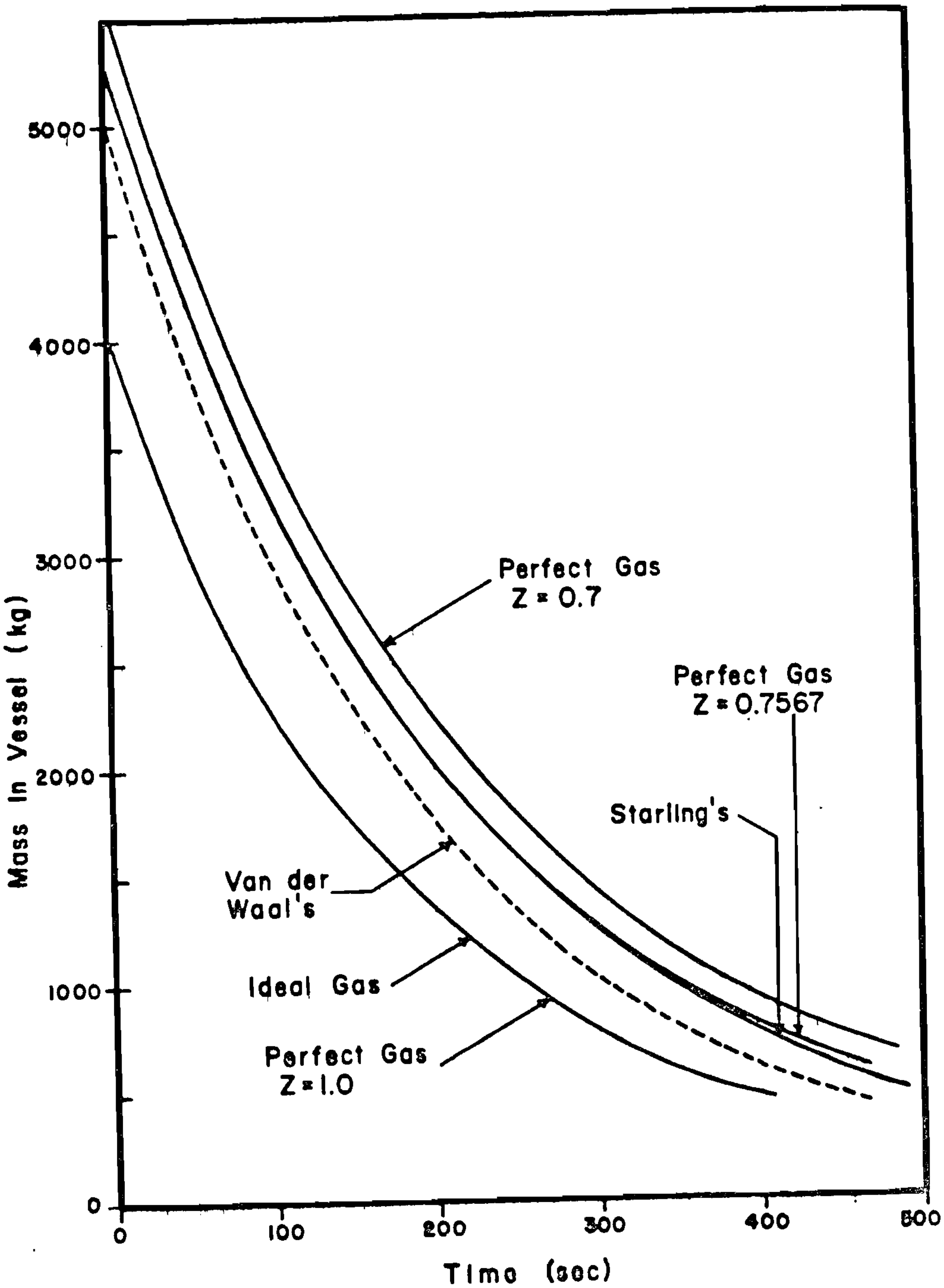

Figure 3: Mass of vapors left in vessel as predicted using various equations of state for propane vapor.

Appendix

Van der Waal's Equation of State:

$$P\ (\rho,\ T) = \frac{\rho RT}{1 - b\rho} - a\rho^2$$

$$h\ (\rho,\ T) = \frac{RT}{1 - b\rho} - RT - 2a\rho + h^o\ (T)$$

$$s\ (\rho,\ T) = -\ R\ \ln \frac{\rho RT}{1 - b\rho} + s^o\ (T)$$

$$C_v\ (\rho,\ T) = -\ R + \frac{dh^o\ (T)}{dT}$$

$$C_p\ (\rho,\ T) = C_v\ (\rho,\ T) - \frac{R^2}{2a\rho\ (1 - b\rho)^2 - RT}\ T$$

$$c\ (\rho,\ T) = \sqrt{\frac{C_p\ (\rho,\ T)}{C_v\ (\rho,\ T)} \left[\frac{RT + 2a\rho\ (1 - b\rho)}{(1 - b\rho)^2}\right]}$$

Starling's Equation of State:

$$P\ (\rho,\ T) = \rho RT + \left(B_oRT - A_o - C_o/T^2 + D_o/T^3 - E_o/T^4\right) \rho^2$$

$$+ \left(bRT - a - d/T\right) \rho^3 + \alpha\ (a + d/T)\ \rho^6$$

$$+ c\rho^3 \left(1 + \gamma\rho^2\right) \exp\left(-\ \gamma\rho^2\right) /T^2$$

$$h(\rho, T) = \left(B_0RT - 2A_0 - 4C_0/T^2 + 5D_0/T^3 - 6E_0/T^4 \right) \rho$$

$$+ \frac{1}{2} (2\ bRT - 3a - 4d/T)\ \rho^2$$

$$+ \frac{1}{5} \alpha\ (6a + 7d/T)\ \rho^5$$

$$+ c \left[3 - \left(3 + \frac{1}{2} \gamma\rho^2 - \gamma^2\rho^4 \right) \exp \left(- \gamma\rho^2 \right) \right] / \gamma T^2$$

$$+ h^0\ (T)$$

$$s(\rho, T) = - R\ \ln\ (\rho\ RT)$$

$$- \left(B_0R + 2C_0/T^3 - 3D_0/T^4 + 4E_0/T^5 \right) \rho$$

$$- \frac{1}{2} \left(bR + d/T^2 \right) \rho^2 + \frac{1}{5} \alpha d\rho^5/T^2$$

$$+ c \left[1 - \left(1 - \frac{1}{2} \gamma\rho^2 - \gamma^2\rho^4 \right) \exp \left(- \gamma\rho^2 \right) \right] / \gamma T^2$$

$$+ s^0\ (T)$$

$$C_v(\rho, T) = - R + \left(6C_0/T^3 - 12D_0/T^4 + 20E_0/T^5 \right) \rho$$

$$+ \rho^2 d/T^2 - \frac{2}{5} \alpha\rho^5 d/T^2$$

$$- 6c \left[1 - \left(1 + \frac{1}{2} \gamma\rho^2 \right) \exp \left(- \gamma\rho^2 \right) \right] / \gamma T^3$$

$$+ \frac{dh^0\ (T)}{dt}$$

$$C_p(\rho, T) = C_v(\rho, T) + \frac{T\left[\left\{\frac{\partial P}{\partial T}\right\}_\rho\right]^2}{\rho^2\left[\left\{\frac{\partial P}{\partial \rho}\right\}_T\right]}$$

$$c(\rho, T) = \sqrt{\frac{C_p(\rho, T)}{C_v(\rho, T)}\left\{\frac{\partial P}{\partial \rho}\right\}_T}$$

where

$$\left\{\frac{\partial P}{\partial \rho}\right\}_T = RT + 2\left(B_oRT - A_o - C_o/T^2 + D_o/T^3 - E_o/T^4\right)\rho$$

$$+ 3\rho^2 (bRT - a - d/T)$$

$$+ 6\alpha\rho^5 (a + d/T)$$

$$+ c\rho^2 \left[3 + 3\gamma\rho^2 - 2\gamma^2\rho^4\right] \exp\left(-\gamma\rho^2\right)/T^2$$

and

$$\left\{\frac{\partial P}{\partial T}\right\}_\rho = \rho R + \left(B_oR + 2C_o/T^3 - 3D_o/T^4 + 4E_o/T^5\right)\rho^2$$

$$+ \left(bR + d/T^2\right)\rho^3 - \alpha d\rho^6/T^2$$

$$- 2c\rho^2\left(1 + \gamma\rho^2\right)\exp\left(-\gamma\rho^2\right)/T^3$$