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Suggestions on the Vapor Pressure Determination of Molten Salts

September 2021

Using the Effusion Method

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SUMMARY

The knowledge of the thermophysical properties of coolant and fuel in molten salts nuclear reactors (MSRs), such as thermal stability and vapor pressure, are of remarkable interest, particularly for simulating safe reactor operations. MSRs use molten salt mixtures as the primary coolant and/or fuel and are expected to operate up to 800°C. With the revived interest in deploying MSRs, complete thermophysical and thermochemical characterization of these materials is of interest to industry, regulators, and researchers. Vapor pressure data for molten salts are scarce in the literature for both pure salts but especially for eutectic mixtures. This report describes the effusion method, which consists of measuring the rate of escape of vapor molecules through a small orifice to determine the vapor pressure which may be useful on compounds such as molten salts. Thermogravimetric analysis records the mass loss as a function of time and temperature. There are two equations that can be used to relate the mass loss rate with the vapor pressure: (1) the Knudsen equation and (2) the Langmuir equation. To apply these equations, the system needs to reach a pseudo (or near) equilibrium condition. Therefore, the experimental conditions must allow the condensed and the vapor/gas phases to be in equilibrium. To accomplish equilibrium-like conditions, the sample must be in an almost sealed cell except for a small orifice from where the vapor escapes. In the Knudsen method, the vacuum is applied to eliminate the effect the presence of other gas molecules could have on the evaporation rate of the sample. However, Langmuir alleged in certain conditions, such as at low temperatures and/or when the vapor pressure is low, a substance's evaporation rate is independent of the presence of vapor around it. For that reason, some researchers do not apply vacuum when using the Langmuir equation when measuring the mass loss of a substance with a predictable low vapor pressure. However, they use a standard substance to parameterize the experimental setup. The use of the Knudsen equation or Langmuir equation will depend on the characteristics of the sample and the availability of an appropriate standard. Some important aspects related to the nature of the samples and vapor pressure measurements are described for future consideration.

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FIGURES

TABLES

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ACRONYMS

HTF	Heat Transfer Fluid
HSC	Enthalpy, Entropy, and Heat Capacity
MSR	Molten-Salt Reactor
TG	Thermogravimetry
TGA	Thermogravimetric Analysis

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1. SUGGESTIONS ON THE VAPOR PRESSURE DETERMINATION OF MOLTEN SALTS USING THE EFFUSION METHOD

Molten-salt reactors (MSRs) are promising nuclear fission reactors in which the primary coolant and/or fuel is a molten-salt mixture. Molten salts are particularly useful as heat transfer fluids (HTFs) due to their high boiling point, wide temperature range in the liquid state, good heat capacity, and thermal conductivity. Furthermore, they were proven to be somewhat resistant to radiation and present a wide range of solubility for actinides. Designing and operating a MSR requires the evaluation of the thermophysical properties of the fuel, coolant, and the container/piping material. Some of these properties are the coefficient of thermal expansion, heat capacity, thermal conductivity, viscosity, melting temperature, and vapor pressure of the fuel and coolant.

Vapor pressure is a measure of the tendency of a substance to change into the gaseous or vapor state, and it increases with temperature. Vapor pressure can also be defined as the pressure exerted by a vapor in thermodynamic equilibrium with its condensed phases at a given temperature in a closed system. The equilibrium vapor pressure is an indicator of a liquid's evaporation rate.

MSRs can operate at higher temperatures than pressurized water reactors, up to 800°C. Therefore, knowing the vapor pressure values of the fuel and coolant in the entire operating temperature range is crucial for the safety and good operation of the reactor. This information will directly influence the selection of the molten-salt system, the design and operation of the reactor, such as temperature and pressure range contemplated in the reactor, the phase composition of the fuel in the reactor vessel, and the emergency plan for a hot-fuel salt-spill accident.

A safety feature of molten-salt nuclear reactors is that in an event of a tank breach, the fuel/coolant will simply freeze at atmospheric temperatures. Since the fuel is not pressurized like traditional reactors, radiation will not disperse into the atmosphere during a breach [1]. However, there is limited data on vapor pressure of molten-chlorides and -fluorides. The purpose of this discussion is to examine a path forward for determining the vapor pressure of common chlorides and fluorides eutectic systems in a wide temperature range.

The consequence of vaporization under dynamic conditions is the substance mass loss. Thus, thermogravimetry (TG), a method based on the continuous measurement of the mass of a sample over time and as a function of temperature, is often employed for conducting vapor pressure measurements. There are several experimental approaches to determine this property, such as the effusion or the transpiration methods. The effusion method is a dynamic technique based on the rate of escape of vapor molecules through a small orifice. It is very useful for measuring low vapor pressures (<100 Pa) [2]. On the other hand, the transpiration method is useful for measuring relatively high pressures [3]. In this method, the sample is heated in an open crucible inside a furnace, and the vapor is transported by a carrier gas at a controlled flow rate. Molten salts are known to have low vapor pressure; therefore, the effusion method is deemed the most suitable approach.

2. EFFUSION METHOD – THEORETICAL BACKGROUND

The effusion technique indirectly determines vapor pressures from measurements of effusion rates through an aperture of small diameter in a sample cell [4] as seen in Figure 1 [5]. In a typical effusion experimental setup, the sample is located in the bottom of a cylindrical tube (i.e. crucible) while kept at constant pressure. To use this method, the vapor and condensed phases must be at or close to equilibrium. The vapor phase of the sample then escapes (effuses) through a small opening in the top of the crucible lid [6]. If the aperture in the lid is sufficiently small, an equilibrium condition will be maintained inside the cell [2]. In thermal equilibrium, mass loss occurs at a constant rate. There are several variants of the effusion method to determine the vapor pressure such as the Knudsen and Langmuir methods.

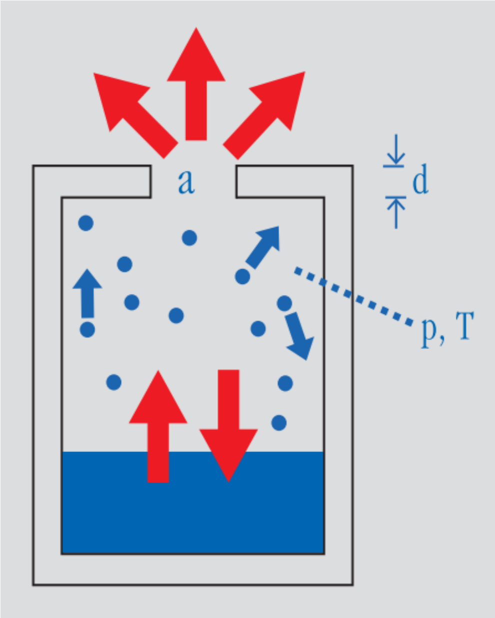

Figure 1. Schematic view of an effusion cell where the gas phase and condensed phase of a substance are depicted in equilibrium [5].

2.1 Knudsen Method

The Knudsen method requires a high vacuum at low to moderate temperatures and isothermal-type measurements. The theory describing the effusion process is based on the kinetic theory of gases, from which Knudsen derived an expression for the isothermal effusion of molecules out of a small orifice in a crucible given a fixed internal pressure (the vapor pressure *P* in this case). The Knudsen effusion method is based on the attempt to allow the condensed and the vapor/gas phases to be in equilibrium in a small chamber, completely sealed except for a very small orifice [7]. The mass (*m*) of the sample sublimated or evaporated from the effusion cell in a period (*t*) is related to the vapor pressure of the condensed phase by Equation ((1) [6]:

$$P = \frac{m}{A_0\, w_0\, t}\sqrt{\frac{2\pi RT}{M}} \tag{1}$$

Where *m/t* is the mass loss rate from the cell; A_0 is the aperture area; *M* is the molecular weight of the compound; *T* is the temperature; *R* is the gas constant; and w_0 is the Clausius probability factor (from 0–1), a measure of the probability that a molecule from inside the cell effuses through the aperture in the lid to the exterior of the cell [4], which is usually calculated using Equation ((2). Where *l* is the length of the effusion orifice and *r* its radius. The cell may also be calibrated using known substances as references.

$$w_0 = \left[1/\left(1 + \frac{3l}{8r}\right)\right] \tag{2}$$

(*P*,*T*) can be used to calculate the enthalpies, $\Delta_{sub}H$, and entropies, $\Delta_{sub}S$, of sublimation of each compound by applying the Clausius-Clapeyron equation, which is typically used to correlate vapor pressures, and it is often written with reference to the sublimation entropy, as shown in Equation (3) [4]. Where P^o is the saturation vapor pressure; *T* is the absolute temperature; and *R* is the universal gas constant.

$$\ln P^o = -\frac{\Delta_{sub}H}{RT} + \frac{\Delta_{sub}S}{R} \tag{3}$$

The Knudsen effusion equation can be applied to a system when the opening in the crucible lid is sufficiently small and the pressure of the system is low enough that the equilibrium between the vapor and condensed phases within the crucible can be maintained [4]. In other words, this is when there are no collisions between the molecules inside the cell or close to the effusion hole and the effused molecules do not perturb the equilibrium between the vapor and the condensed phases. These conditions are met when the surface area of the condensed phase is considerably larger than the aperture area in the lid [2].

2.2 Langmuir Effusion Method

The Langmuir effusion equation can be applied for mass loss rate data obtained under ambient conditions (not vacuum) in certain conditions. Langmuir alleged "in certain conditions, such as at low temperatures and/or when the vapor pressure is low, we may consider the actual rate of evaporation of a substance is independent of the presence of vapor around it. That is, the rate of evaporation in high vacuum is the same as the rate of evaporation in presence of saturated vapor"[8].

To use the experimental setup at ambient conditions, it is required to premeasure the evaporation mass loss rate of a known reference substance in an isothermal regime. Then a generalization of the Langmuir equation for free vaporization can be applied—see Equation (4). Where *a* is the area of the effusion hole; $\left|\frac{dm}{dt}\right|_T$ is the mass loss rate; and P_T is the vapor pressure both at a given temperature.

$$\log P_T = s\ \log\left(\frac{1}{a}\left|\frac{dm}{dt}\right|_T\right) + b \tag{4}$$

The parameters *s* (slope) and *b* (y-axis intercept) can be determined after linearization of Equation (4) by measuring a chemical substance with a known vapor pressure curve. The two parameters *s* and *b* are then known, and the vapor pressure of an unknown substance can be determined under identical experimental conditions.

The Clausius-Clapeyron equation can be used to determine the enthalpy (ΔH) of the phase transition or to check the vapor pressure measurement for a known value of ΔH. Table 1 shows a comparative of the two experimental approaches proposed herein to determine the vapor pressure.

Table 1. Comparative of several methods used to calculate vapor pressure.

Method	Pressure	Temperature program	Reference material	Equation	Temperature range (experiments from literature)	Notes	Reference
Knudsen	Vacuum	Isotherms	No	$P = \frac{m}{A_0\, w_0 t}\sqrt{\frac{2\pi RT}{M}}$	297 to 432 K	Vacuum 10–5 mbar (outside the Knudsen cell)	[2,4,6,9]
Langmuir	Ambient	A series of isothermal segments (10 min) in steps of 10 K	Yes (e.g., benzoic acid)	$\log P_T = s\ \log\left(\frac{1}{a}\left\|\frac{dm}{dt}\right\|_T\right) + b$	410 to 490 K	The gas flow ensured that the concentration of the sample vapor outside the crucible was as low as possible[a]. N_2 at 60 mL /min as purge gas	[5]

3. VAPOR PRESSURE EXPERIMENTS - MOLTEN SALTS

Vignarooban et al. [10] measured the vapor pressure of the ternary eutectic mixture, NaCl-KCl-$ZnCl_2$, at various temperatures (250–1000°C). The experiment configuration includes a quartz test tube, a thermocouple, a condenser, and a pressure gauge along with access to a vacuum pump. The test cell was vacuumed to remove the air before heating the sample. Vapor pressure values were recorded at different temperatures. Calibration was performed by measuring the vapor pressure for $ZnCl_2$ and comparing the data with the vapor pressure values in the literature. Direct methods, such as the one used by Vignarooban et al. [10], where the pressure is determined by measuring the force exerted on a known area are not very precise with pressures below 2 Pa ($<10^{-2}$ mmHg).

Zhang et al. [2] determined the vapor pressure for binary and ternary metal chloride systems using the Knudsen effusion method at 800, 830, and 850°C. They assumed the mixed condensed and vapor phases of KCl-NaCl exhibit the same behavior with ideal solution and ideal gas since the components have similar molecule structures and vapor pressure values. The vapor pressure values of several fluorides and chlorides in the molten state are shown in Table 2.

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[a] Important to reach equilibrium conditions.

Table 2. Vapor pressure values for some common molten salts.

Salt	Melting temperature (°C)	Vapor pressure (bar)	Reference
Potassium fluoride (KF)	858	0.065 (at 1200°C)	[11]
Potassium chloride (KCl)	770	0.18 (at 1200°C)	[11]
Sodium chloride (NaCl)	800.1°C	0.117 (at 1200°C)	[12]
NaCl-KCl-$ZnCl_2$ (13.4–33.7–52.9 mol%)	204°C [13]	0.71 (800°C)	[10]

For a given reaction, Equation (5), the equilibrium constant K can be calculated as in Equations (6) and (7). Vapor pressures p can be calculated by using the reaction equation for the vaporization reaction concerned [14]. For example, for pure sodium chloride, the equilibrium is NaCl = NaCl(g). The activity a_{NaCl} of pure sodium chloride is 1, and thus, the vapor pressure in bar is equal to the equilibrium constant according to Equations (7) and (8). Where *[A]* is the activity or partial pressure of species A; a is the stoichiometric coefficient of species A in reaction; R is the gas constant (1.987 cal/K·mol = 8.314 J/K·mol); and T is the temperature in Kelvin [15].

$$aA + bB + \cdots = cC + dD + \cdots \tag{5}$$

$$K = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b} \tag{6}$$

$$\ln K = \frac{-\Delta G_{reaction}}{RT} \tag{7}$$

$$K = \frac{p_{NaCl(g)}}{a_{NaCl}} = p_{NaCl(g)} \tag{8}$$

If a substance vaporizes into several components, all of them must be taken into consideration. The total vapor pressure is then the sum of all the individual partial pressures if the gas phase behaves ideally. Figure 2 and Figure 3 show calculated equilibrium constants for chloride- and fluoride-based fuel salts of interest in developing MSRs. The presence of UCl_4 or $PuCl_4$ in the salt will result in volatilization of the components prior to volatilization of the trivalent chlorides. Also, of interest is the vaporization of fission product such as iodine.

In general, it is predicted the main components of MSR fuel will not be volatile in the operating range of a reactor (~500–800°C). However, the behavior of the fission products and corrosion products is lesser known. Volatility of salt components can affect thermophysical property measurements, such as specific heat capacity, which is commonly calculated using a constant mass. The stability of salts within a temperature range of interest is not only important for modeling and simulations but also for accurate determination of thermophysical properties and predicting phase stability during salt-spill events.

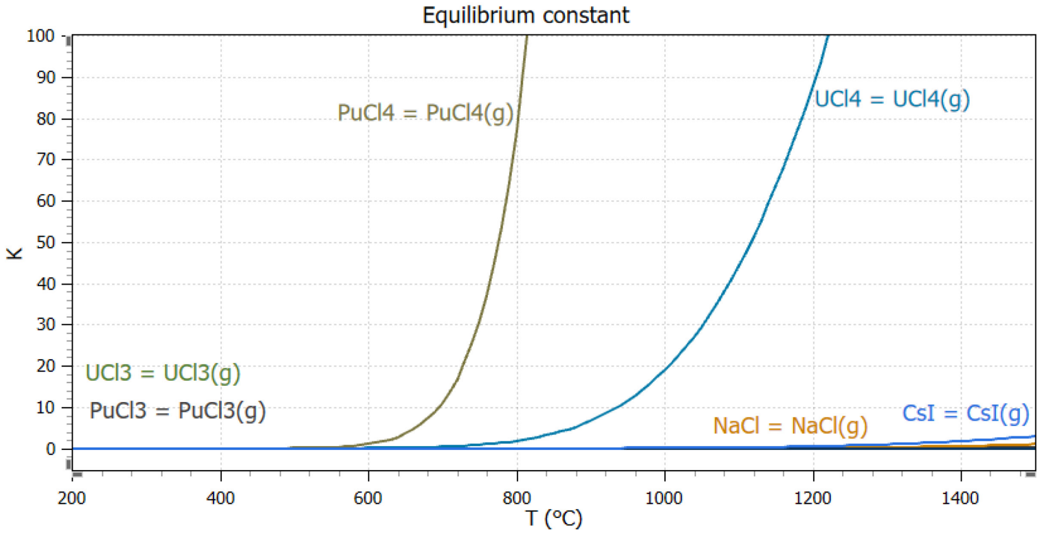

Figure 2. Graphical results from reaction equation calculations performed in Enthalpy, Entropy, and Heat Capacity (HSC) Chemistry 9 for some chloride-based fuel salts of interest in MSRs [16].

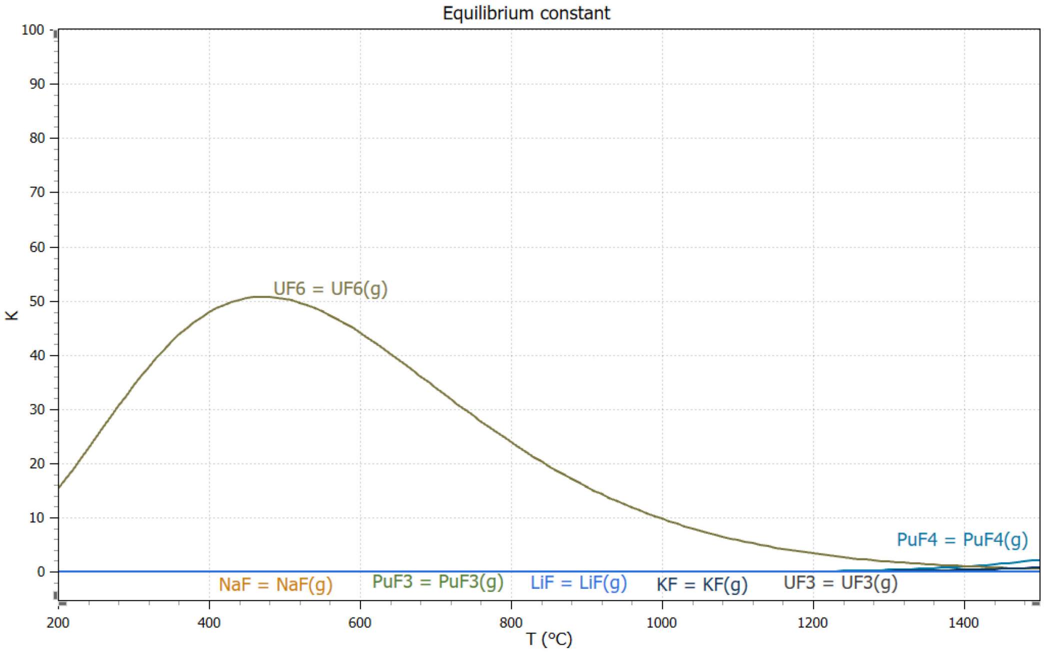

Figure 3. Graphical results from reaction equation calculations performed in HSC Chemistry 9 for some fluoride-based fuel salts of interest in MSRs [16].

4. EXPERIMENTAL ASPECTS TO CONSIDER

The mass loss of any liquid during a thermogravimetric analysis (TGA) may depend on a variety of parameters. It is important to consider evaporation and thermal decomposition can take place simultaneously at certain temperatures. The rate of mass loss by thermal decomposition is independent of the crucible's geometry, type of gas, or flow rate. However, the evaporation rate depends on the sample surface exposed, sample size, crucible geometry, and the diffusion coefficient of the vapor in the carrier gas. The rate of mass loss due to evaporation should be faster with He then with N_2 as carrier gas since, typically, the diffusion in He is about three times faster than in N_2. If decomposition takes place alone, the mass loss rate does not depend on the gas [17].

To discriminate between evaporation or decomposition using TGA, several experiments could be run such as 1) varying the heating rate (e.g., 2–10 K/min) using a constant flow rate, 2) varying the inert gas flow rate, or 3) using different inert gases such as N_2 and He.

To study the influence of the surface exposed of the condensed phase on the evaporation rate, crucibles with different diameters (open crucibles) can be used. These experiments can provide interesting information which can be related to the extent of the surface expose which might be of importance during a salt spill. By running multiple experiments with varying parameters, we can obtain vapor pressure and evaporation rate in different conditions.

In regard to vapor pressure measurements, an important factor that could affect the measurement is the temperature stabilization time at the beginning of an isotherm. This factor is specific for each TGA setup. It means the recorded data of the mass loss during the stabilization period should be excluded from the data treatment [18].

5. ASPECTS FOR FUTURE CONSIDERATION

Below is a series of aspects to be considered in the future:

- How does a eutectic mixture evaporate? Is it a congruent evaporation? What is the vapor phase composition?
- Are the formulas of Knudsen and Langmuir applicable to mixtures? Can we consider them ideal solutions and ideal gases?
- Would it be useful to determine the vapor pressure of the pure components of the mixture? Is the equipment sufficiently sensitive to determine low vapor pressures? How sensitive? Minimum mass to lose to be sensed by the equipment?
- Since the diameter of the orifice in Netzsch effusion cells is 2.9 mm (vs. 12 mm diameter crucible), is the orifice small enough to maintain an equilibrium condition inside the cell? The escaped molecules should not disturb the equilibrium between the condensed phase and the vapor (for the Knudsen method). If that is not the case, a cell with different dimensions should be acquired, to be able to apply the Knudsen method.
- If we were to apply Langmuir method, which calibration substance should we use? It should have a similar behavior to our samples and would need to be measured in the same temperature range. We cannot use benzoic acid due to its low boiling point of 249 °C.

6. CONCLUSIONS

The revived interest in MSRs increases the need for complete thermal characterization of molten salts. Vapor pressure data for molten salts are scarce in the literature for both pure salts but especially for eutectic mixtures. This report proposes to apply the effusion method for determining the vapor pressure of pure salts and eutectic mixtures with interest in the field of the MSRs. The equation and approach selected will depend on the characteristics of the salt and the availability of an appropriate standard needed for Langmuir approach.

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