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# Volatility Rate of Isopar® L, Benzene, Salt Solution, Potassium Tetraphenyl Borate (KTPB), and their Mixtures by ASTM Method E 2008-04

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**Abstract:** Data are provided for the relative rate of volatility of Isopar® L, CSSX solvent, and salt solution in relation to benzene. The results also include rates for mixtures of the various species and the impact of tetraphenylborate on the volatility. The results are consistent with the expected behavior in that the component with a lower boiling point volatizes faster than a component with a higher boiling point. Fick's diffusion law explained the data well and it predicted the diffusivity of Isopar® L (a mixture of hydrocarbons) intermediate temperatures between 35 and 70°C. Inspection of the data shows the volatility of Isopar® L is approximately 1/10th that of the salt solution and approximately 1/100th that of benzene under comparable conditions at the temperatures studied. The results can be used to rank the relative volatility rate of these substances.

**Keywords:** Evaporatin; Gas diffusion; Immiscible; TGA

## INTRODUCTION

The Savannah River Site stores several millions gallons of radioactive supernatant in storage tanks. The liquid waste is toxic, caustic, and radioactive. The supernatant radioactivity is due to the isotopes of cesium. These isotopes are the result of nuclear fission of the isotopes of uranium and plutonium.

The Department of Energy (DOE) identified the Caustic Side Solvent Extraction (CSSX) process as the preferred technology to remove cesium

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from radioactive waste solutions at the Savannah River Site (SRS) (1). The solvent extraction process generates two effluent streams: a decontaminated salt solution (DSS) depleted in radio-cesium, and a strip effluent (SE) containing concentrated radio-cesium removed from the DSS stream. These streams pass through coalescers and decanters to remove suspended solvent droplets, reducing solvent carry-over to the downstream facilities. The recovered solvent becomes available for reuse in the solvent extraction process. The DSS stream transfers to Tank 50H and from Tank 50H to the Saltstone Production Facility. The SE stream transfers to the Defense Waste Processing Facility (DWPF), where the radio-cesium is vitrified with sludge waste. Organic material from the CSSX process may end up in Tank 50H.

The CSSX solvent contains four components (2). One component, Isopar® L, is volatile and may be a flammability hazard in downstream processes (due to loss of inert gas purging and/or ventilation). Gross estimate of the diffusivity of Isopar® L by calculation methods can be suspect since Isopar® L is a mixture of $C_{10}$, $C_{11}$, and $C_{12}$ linear hydrocarbons. Literature survey has revealed several theoretical calculations for estimating evaporation rates (3–7). Many of these calculations focused on pure components (3,4) while others are empirical equations based on the purge or free-gas flow over the evaporating liquid (5,6,7).

For experimental estimating evaporation rate from liquids, the American Society for Testing and Materials (ASTM) has developed two methods: E 2008-04, "Standard Test Method for Volatility Rate by Thermogravimetry (8)," and "Standard Test Method for Evaporation Loss of Lubricating Oils by Thermogravimetry (TGA) Noack Method, D 6375-05 (9)," for measuring the volatility rate of organic materials. The method utilizes a thermogravimetric analyzer that monitors weight loss under isothermal conditions. Method D 6375-05 works well for low-volatility substances like engine oils, while method E 2008-04 works well for high-volatility substances or low-molecular-weight compounds. In this work, method E 2008-04 was chosen for analyzing the volatility rate of small molecules, such as water and benzene. Although the method does not directly yield the absolute volatility rate, it does provide a volatility ranking when comparisons are made against a standard. This paper provides details of the measurements obtained.

## EXPERIMENTAL

This effort used a salt simulant solution (SS) that closely resembles waste tank supernatant. Table 1 lists the chemical composition for this salt solution (10). This effort also used full CSSX solvent (2), the composition of

**Table 1.** Composition of simulated salt solution

| Component | Concentration (molar) |
|---|---|
| $Na^+$ | 5.6 |
| $K^+$ | 0.015 |
| $OH^-$ | 2.0 |
| $NO_3^-$ | 2.0 |
| $NO_2^-$ | 0.49 |
| $AlO_2^-$ | 0.29 |
| $CO_3^{2-}$ | 0.15 |
| $SO_4^{2-}$ | 0.14 |
| $Cl^-$ | 0.023 |
| $F^-$ | 0.027 |
| $PO_4^{3-}$ | 0.007 |
| Oxalate | 0.008 |
| $SiO_3^{2-}$ | 0.03 |
| $MoO_4^-$ | 0.00007 |

which is shown in Table 2. Other chemicals (i.e., sodium tetraphenylborate and benzene) met American Chemical Society reagent grade standards.

The thermogravimetric analyzer equipment used for this method takes 20 minutes to reach isothermal conditions at a given temperature. Sample is lost during this adjustment. In order to have enough of each component in a mixture when the instrument reached steady state conditions, sufficient amounts of each component was added to the crucible. The mass ranges of each component are listed in Table 3. These masses represent optimal amounts required for the TGA unit to detect after the instrument reached steady state conditions.

The thermogravimetric method for measuring the rate of evaporation of liquids requires a small, inert crucible with a 0.35-mm diameter hole in

**Table 2.** Composition of CSSX solvent

| Component* | Concentration (molar) | Concentration (wt % solvent) |
|---|---|---|
| Extractant (BOBCalixC6) | 0.007 | 0.9 |
| Modifier (Cs-7SB) | 0.75 | 29.8 |
| Tri-n-octyl amine | 0.003 | 0.1 |
| Diluent (Isopar® L) | (balance) | 69.2 |

*BOBCalixC6 = Calix[4]arene-bis(*tert*-octylbenzo-crown-6); Cs-7SB = 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol.

**Table 3.** The range of masses used for each of the components

| Component | Minimum (mg) | Maximum (mg) |
|---|---|---|
| Benzene | 5 | 26 |
| Solvent (CSSX) | 25 | 28 |
| Isopar® L | 0.5 | 23 |
| Salt Solution | 26 | 53 |
| KTPB in Salt Solution | 3000 ppm | 3000 ppm |

the lid. The manufacturer recommended by ASTM is no longer in business. Therefore, we purchased crucibles with outer diameters of 7.28 mm, then used 0.34-mm drill bits with guiding bushings and perforated several of the cups to obtain an average hole diameter of 0.45 ± 0.03 mm.

The cups were filled with the liquids listed in Table 3. All weights listed in Table 3 are given in mg. Please note there is no relationship between these weights and the expected concentrations in the tank. An illustration of the cup used in these experiments is shown in Figure 1.

## RESULTS

### Consistency with Previous Testing

Evaporation testing was conducted with de-ionized water. The evaporation data from water was plotted along with water evaporation data published in ASTM standard E 2008-04 (8) in Fig. 2. A visual inspection of Fig. 2 shows that the measured water evaporation rate is within agreement with the ASTM data except at 72°C where our data clearly diverges from the ASTM data. Given the fact that the average orifice diameter of our crucibles was larger than recommended by ASTM (8), the large divergence at the higher temperature may be expected.

### Evaporation Rate of Pure and Mixed Components

A typical evaporation curve of a mixture of benzene and Isopar® L is shown in Fig. 3. Looking at Fig. 3, there are two intercepting lines over the time period measured. The line with the highest slope corresponds to the evaporation of benzene. Note the evaporation rate is constant (linear profile) over the observed time scale. The other line corresponds to the evaporation of Isopar® L. The thin lines below the thick curve (representing actual data) are for estimating the slope and therefore, the evaporation rate. This was done for all the pure components and their mixtures evaporation data. A

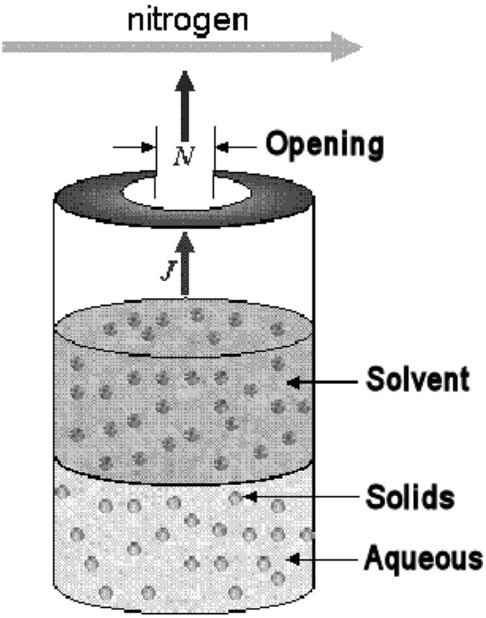

***Figure 1.*** Schematic of experimental configuration. J is flux from the liquid surface; N is flux from opening.

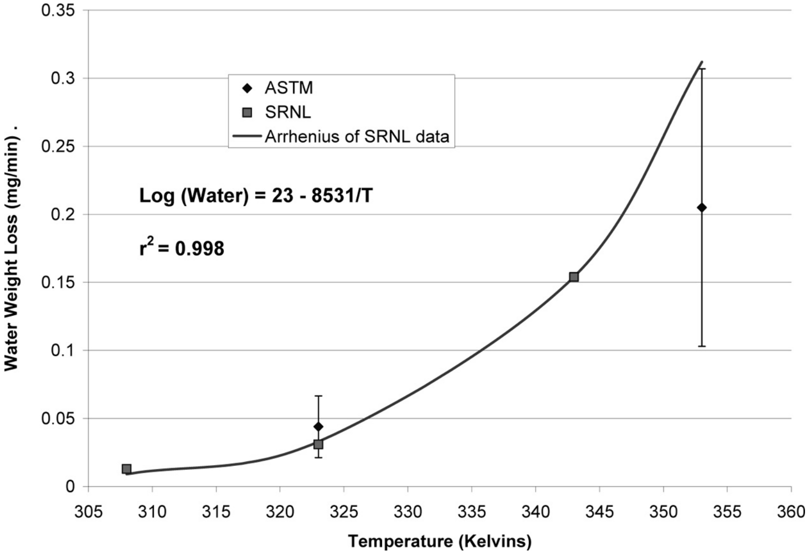

***Figure 2.*** Volatility of water data from this study and comparison to ASTM data.

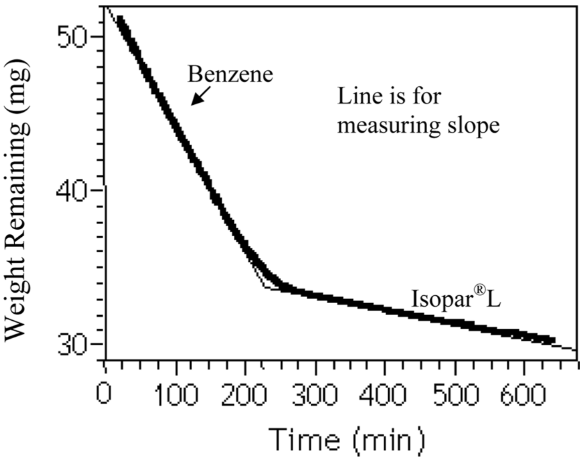

***Figure 3.*** Volatility of salt solution (with 3000 ppm KTPB) containing Isopar® L and Benzene at 35°C.

summary of the evaporation rate for the pure component and their mixture is shown in Table 4. A visual inspection of Table 4 clearly shows that benzene evaporates faster than water or salt solutions and that water evaporates faster than Isopar® L. As expected, benzene, due to its high vapor pressure and high diffusivity, evaporates faster than water and Isopar® L. A plot of the effect of temperature on the evaporation rate of the pure components is shown in Figure 4. Since evaporation measurements can only provide a

**Table 4.** Flux of benzene, Isopar® L, water, salt solution, and their mixtures (moles/cm$^{2*}$sec)

| | 308 (K) | 323 (K) | 348 (K) |
|---|---|---|---|
| Benzene | 1.06E-05 | 2.35E-05 | 6.60E-05 |
| Benzene in SS (= Salt Solution) | 1.24E-05 | 2.77E-05 | |
| Benzene in SS + KTPB + Isopar® L | 1.09E-05 | 2.53E-05 | |
| Benzene in SS + Isopar® L | 8.06E-06 | 2.34E-05 | |
| Benzene in Isopar® L | 7.79E-06 | 1.49E-05 | |
| Isopar® L | 7.76E-07 | 1.73E-06 | 5.36E-06 |
| Isopar® L in CSSX | 9.35E-07 | 1.56E-06 | 5.61E-06 |
| Water (Control Data) | 7.59E-06 | 1.80E-05 | 8.98E-05 |
| SS | 5.70E-06 | 1.33E-05 | 3.43E-05 |
| SS + Isopar® L | 4.65E-06 | 1.24E-05 | 3.15E-05 |
| SS + Benzene | 5.34E-06 | 1.28E-05 | 3.72E-05 |
| SS + KTPB + Isopar® L + Benzene | 5.24E-06 | 1.33E-05 | 3.43E-05 |
| SS + Isopar® L + Benzene | 5.06E-06 | 1.28E-05 | 3.43E-05 |

relative evaporation rate rank of unknown substance to known standards such as benzene, there is a need to also determine or estimate the diffusivity of an unknown sample given that its vapor pressure is known. Once the diffusivity and the vapor pressure of an unknown substance are determined, the evaporation rate can be calculated.

## PREDICTING THE EVAPORATION OF LIQUIDS THROUGH AN ORIFICE OF A CRUCIBLE

There are at least four mass-transfer mechanisms for a gas to escape through an orifice: Knudsen diffusion, which applies when the gas molecules' mean free path is greater than the diameter of the orifice; molecular diffusion, which is driven by concentration gradient; viscous diffusion, described by Poiseuille's Law; and surface diffusion, for transport along the walls of the orifice. We estimated that viscous flow and surface diffusion contributions to the mass transfer are negligible.

With respect to Knudsen diffusion, if the diameter of the opening becomes very small, one expects Knudsen diffusion to dominate. This is the case only if the opening is small relative to the mean free path for diffusion. The mean free path of the gas molecules in these crucibles is much less than the diameter of the pinhole. The mean free path, $\lambda$, of the gas molecules is shown in Equation 1 (11).

$$\lambda = \frac{kT}{\pi\sigma^2 P_{saturation}\sqrt{2}} \tag{1}$$

In this expression, "$k$" stands for the Boltzmann constant, "$T$" is the temperature (in Kelvin), "$\sigma$" is the molecular diameter (in meters), and "$P_{saturation}$" is the saturation pressure inside the crucible (in Pascals). For benzene, the molecular diameter is $2.55 \times 10^{-10}$ m (12). At 35°C, and a pressure of 4,417 Pascals the mean free path is about $7.6 \times 10-7$ meters. This path length is very small compared to the diameter of the orifice ($4.5 \times 10^{-4}$ m). Therefore, the flow of gas out of the orifice is not well described as a Knudsen diffusion problem.

The rate at which a gas escapes the crucible is inversely proportional to the resistance of evaporation and diffusion through the hole. The reciprocal of the resistance for escaping the crucible is the sum of the reciprocal of the resistance for evaporation, convection, and diffusion through the hole. If molecular diffusion through the hole is the rate-limiting process, then the weight loss rate per unit temperature should be proportional to the absolute temperature raised to the 1/2 to

3/2 power, consistent with the functional form of the expression of the Gilliland method (13) for binary diffusivity of gases:

$$D = 0.0043\frac{T^{3/2}}{P(V_1^{1/3} + V_2^{1/3})^2}\sqrt{\frac{1}{M_1} + \frac{1}{M_2}} \tag{2}$$

In this expression, "$T$" stands for absolute temperature, "$P$" for absolute pressure, "$V_i$" stands for collision volume (molecular volume), and "$M_i$" stands for molecular weight. As can be seen, the diffusivity varies with temperature to the power of 3/2. If we assume unity for the coefficients, the expression simplifies to a difference between the saturation pressure of the liquid and the actual partial pressure above the liquid. The flux of gas going through the orifice is shown in Equation 3 (11).

$$N_i = \frac{ADP}{RT\Delta z(1-\beta)}LN\frac{1-(P_2/P)(1-\beta)}{1-(P_1/P)(1-\beta)} \tag{3}$$

The symbol "$N_i$" stands for the flow of gas "$i$" diffusing through the orifice (please note this flux does not necessarily equal the flux "$J_i$" in Equation 4), the symbol "$A$" stands for the area of the orifice, "$D$" for the diffusivity, "$P$" for the total pressure (101325 Pa), "$\Delta z$" for the thickness of the crucible + s walls ($\approx$0.162 mm), "$\beta$" is the fraction of the flux of nitrogen gas (purge gas) moving opposite to the gas escaping from the crucible, and "$P_1$" is the partial pressure in the crucible near the orifice and $P_2$ is the partial pressure outside the crucible near the orifice $\approx$0. Equation 5 comes from a 1-dimensional analysis; therefore, caution is in order. The low value for the length-to-diameter ratio of the orifice makes "$\Delta z$" an approximation. As the diameter shrinks and the gas flow declines, the configuration approaches a sealed vessel with the behavior approaching equilibrium.

One then expects the pressure—in this case the saturation pressure ($P_{\text{saturation}}$)—to obey the Clausius-Clapeyron equation (13) for equilibrium conditions,

$$Ln\left(\frac{P^2_{saturation}}{P^1_{saturation}}\right) = -\frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{4}$$

If evaporation is diffusion controlled, then it is a straightforward exercise to compute the diffusivity of substances with unknown gas diffusivity using the TGA data from the E 2008–04 method, as shown in Equation 5,

$$D_{unknown} = (D_{known})_{literature} \times \left(\frac{Flux_{unknown}}{Flux_{known}}\right)_{measured\ by\ TGA} \times \left(\frac{Ln(1 - P_{known}/101325)}{Ln(1 - P_{unknown}/101325)}\right)_{literature} \tag{5}$$

In equation 5, the symbol "$P_{unknown}$ or $P_{known}$" stands for equilibrium pressure as given by the Clausius-Clayperon equation. In equation 5, it is assumed that the path length resistance (diffusion length and any hydrodynamics resistance) is the same for the different volatile chemicals. To ascertain which mechanism controls the rate of gas escape in these experiments, we regressed the rate of weight loss as a function of both the absolute temperature and the reciprocal of the absolute temperature. Figure 5 shows the weight loss rate of benzene as a function of temperature. The same figure shows a prediction curve (as a solid line) obtained from regression of the data. As can be seen, the prediction curves fit the data well ($r^2 = 0.99$ or greater). The prediction curve in Fig. 5 is based on the function log (weight loss) versus T. According to the theory of binary diffusion for gases (as well as empirical correlations), the diffusivity is a function of temperature (in Kelvin) to the 0.5 to 1.5 power. If the escape rate from the crucible is diffusion controlled, then the slope of the line in Fig. 5 should approach 0.5 to 1.5. The calculated slope is 2. This value is above the expected value of 0.5 to 1.5 for a diffusion-controlled gas flow. Despite the numerical disagreement in the calculated exponent of temperature and the theory, we believe the evaporation process is diffusion controlled.

From Fig. 5 the slope of the plot was used to calculate the activation energy of benzene vaporization and from the slope the activation energy

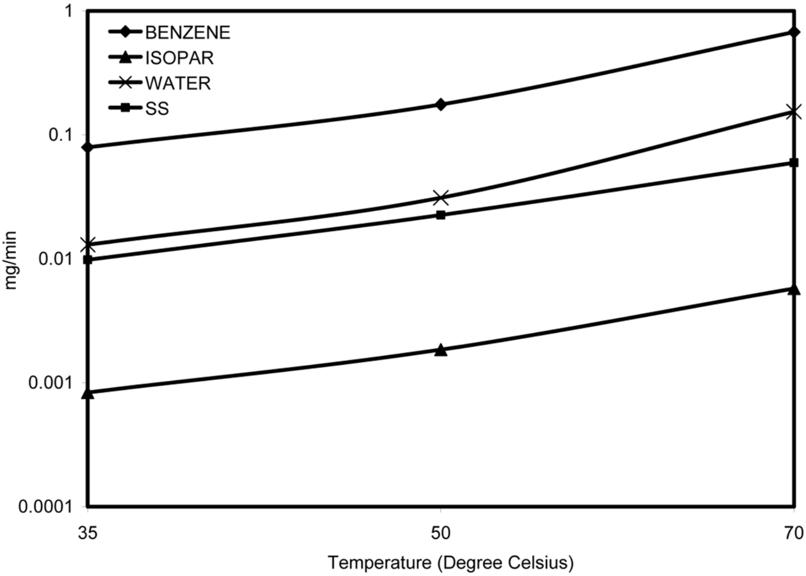

***Figure 4.*** The Volatility rate of the pure component as a function of temperature.

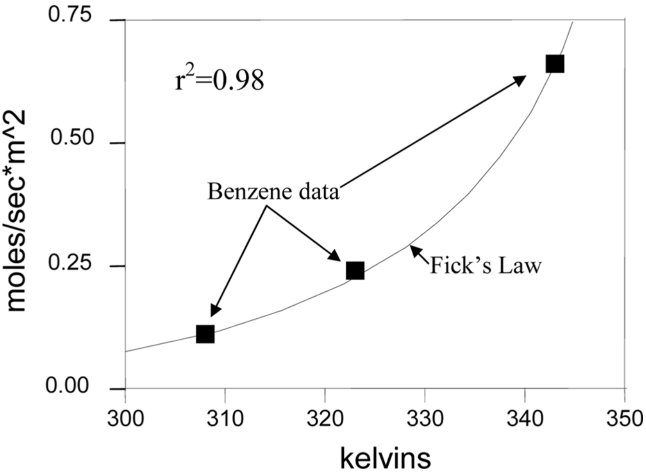

***Figure 5.*** Volatility of benzene compared to molecular diffusion.

measured 46 kJ/mol (= 5521 K × 0.008314 J/(mol*K)). The enthalpy for benzene vaporization is 33.83 kJ/mol at 25°C (14). The additional activation energy may result from hydrodynamics effects at the entrance of the orifice. Therefore, the evaporation rate measured by the TGA is limited by diffusion through the orifice.

To determine the diffusivity of Isopar® L, the vapor pressure and diffusivity constants for the standard must be determined. Table 5 lists the vapor pressure and diffusivity (in air) of benzene, water, and Isopar® L (diffusivity is not provided) as a function of temperature. The benzene and water data in Table 5 was in conjunction with Equation 3 to predict the water evaporation rate. Table 6 shows the water evaporation rate predicted from Eq. 3 and the measured water evaporation rate from this test. As can be seen from Table 6, there is closer agreement between prediction and the data at temperatures less than 50°C. The divergence between

**Table 5.** Vapor pressure and diffusivity constant (in air) of benzene, water, and Isopar® L (diffusivity not provided for Isopar® L) as a function of temperature

| Temperature (K) | kPa water | kPa Benzene | kPa Isopar® L | $cm^2/sec$ water | $cm^2/sec$ benzene |
|---|---|---|---|---|---|
| 308 | 5.58 | 20.34 | 0.186 | 0.272 | 0.099 |
| 323 | 12.29 | 32.49 | 0.477 | 0.296 | 0.107 |
| 343 | 31.27 | 46.44 | 1.437 | 0.328 | 0.119 |

**Table 6.** Prediction of water evaporation rate through the perforated steel crucible

| Temperature (K) | mol/cm$^2$ sec Benzene | mol/cm$^2$ sec water | mol/cm$^2$ sec water predicted | % difference |
|---|---|---|---|---|
| 308 | 1.06E-05 | 7.59E-06 | 7.70E-06 | 1.8 |
| 323 | 2.35E-05 | 1.80E-05 | 1.92E-05 | 6.1 |
| 343 | 6.60E-05 | 8.98E-05 | 5.26E-05 | 41.3 |

**Table 7.** Prediction of Isopar® L diffusivity constant in air as a function of time

| Temperature (K) | mol/cm$^2$ sec Benzene | mol/cm$^2$ sec Isopar® L | cm$^2$/sec Isopar® L calculated |
|---|---|---|---|
| 308 | 1.06E-05 | 7.00E-08 | 0.076 |
| 323 | 2.35E-05 | 1.90E-07 | 0.080 |
| 343 | 6.60E-05 | 5.20E-07 | 0.084 |

prediction and the measured data is significant (41% difference) at 70°C. This indicates that using a standard like benzene with known diffusivity and vapor pressure values and the use of Eq. 3 can be used to predict the evaporation and/or diffusivity of an unknown gas substance if the vapor pressure of the unknown gas is known.

To estimate the diffusivity of Isopar® L in air, we used the data for benzene given in Table 6, the measured Isopar® L evaporation flux, and Eq. 5, to determine the diffusivity. The results are shown in Table 7. Looking at Table 7, the calculated diffusivity of Isopar® L are slightly higher than expected by no more than 35%. The calculated diffusivity shows that this method and Eq. 5 provide a means for estimating the diffusivity of gases in air.

## CONCLUSION

Data are provided for the relative rate of volatility of Isopar® L, CSSX solvent, and salt solution in relation to benzene. Results also include rates for mixtures of the various species and the impact of tetraphenylborate on the volatility. The results are consistent with the expected behavior in that the component with a lower boiling point volatizes faster than a component with a higher boiling point. Fick's diffusion law described the data well and it predicted the diffusivity of Isopar® L (a mixture of hydrocarbons) at intermediate temperatures between 35 and 70°C.

Inspection of the data shows the volatility of Isopar® L is approximately 1/10th that of the salt solution and approximately 1/100th that of benzene under comparable conditions at the temperatures studied. The relative rate results can be used to rank the relative volatility rate of these substances in the tank farm.

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