An impurity model for LAr detectors

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Outline

• Motivation
• Model description
• Measurement of Henry’s coefficients for oxygen
• Determination of impurity leak rate
• Summary
Motivation

- Impurities in LAr ($O_2$, $H_2O$, etc.) reduce charge and light signals
- Ultra-high purity LAr (<1 ppb) required for long drift distances (> 3.6 m)
- A model is desired for understanding the dynamics of impurities in LAr
- Important for detector optimization and operation

Ref.: NIM 135 (1976) 151
Seven processes are considered for the impurity dynamics:
Model description – overview

- Ordinary differential equations for each process
- E.g., for process #1:

\[
\begin{align*}
\frac{dn_{i,g}}{dt} &= n_g \left( -n_{i,g} k_{dis} + n_{i,l} k_{dev} \right) + c_{i,g} \frac{dn_g}{dt}, \\
\frac{dn_{i,l}}{dt} &= -\frac{dn_{i,g}}{dt}
\end{align*}
\]

\( n_{i,l}, n_{i,g} \): amount of impurity in liquid, gas
\( n_g \): amount of argon in gas
\( c_{i,l}, c_{i,g} \): concentration in liquid, gas
\( k_{dis}, k_{dev} \): dissolution, devolution rates
The prediction from the model

- The full model is constructed by summing up all processes
- Concentrations are in non-linear 3rd order differential equations
- By reducing the sampling (#6) and outgassing (#7) processes, analytical solutions:

\[
c_{i,l}(t) = c_{ss,l} + C_1 e^{-k_F t} + C_2 e^{-k_S t},
\]
\[
c_{i,g}(t) = c_{ss,g} + C_3 e^{-k_F t} + C_4 e^{-k_S t}
\]

Ultimate concentrations
Fast Component (~ secs)
Slow Component (hrs)

- Analyzing \( k_S \):

\[
H = \frac{\text{Cleaning rate of argon}}{\text{Evaporation rate of argon}}
\]

Heating power to the LAr

\[
H \equiv c_{ss,g} \quad \text{Definition of the Henry’s coefficient (at equilibrium)}
\]

The model predicts a way to measure the Henry’s coefficient
The BNL 20-L LAr test stand

- For studying basic properties of LAr: measured longitudinal diffusion of electrons (NIMA 816 (2016) 160)
- Gas purification only
- Additional heating power can be varied 0-150 W
- Oxygen and water concentrations measured by sampling LAr into gas analyzers (0.2 ppb precision)

Details: JINST 16 06 t06001
Henry’s coefficient for oxygen ($H_{Oxygen}$)

- Data used for analysis selected based on slow control data (LAr level, heater temperature, etc.)
- Cleaning rates measured at different heating powers

$$H = \frac{\text{Cleaning rate of argon}}{\text{Evaporation rate of argon}} = \frac{r_{cln}}{r_{evp}}$$

- $H_{Oxygen} = 0.84 \pm 0.04$, consistent with literature
Understanding the water data ...

- The water case is more complicated
  - outgassing process (#7) can’t be ignored
  - adsorption on surfaces may explain the fast cleaning observed in data

- More data are needed

$H_{\text{water}} = 3 \times 10^{-9}$ from NIST REFPROP
- from equation of state calculation
- Water vapor pressure $\sim 10^{-22}$ bar (at 90 K)
  (extrapolated from empirical equations)

Water concentration data (Feb. 2016 data set)
Another application - Numerical fit to the data

- The full model is numerically fitted to the data
- The measured Henry’s coefficient is used;
- The purification off regions also fitted

- The leak rate can be determined:
  - \( \approx 5 \times 10^{-6} \) mole/h with purification off;
  - \( \approx 10^{-7} \) mole/h with purification on;
  - It is further reduced when heating power is increased.

- The model fits the data very well
Keeping impurities away from the LAr

- The dependence of leak rate on the input heating power can be explained by a simple diffusion model:

\[ c_{i,g}(x) = C \cdot e^{-\left(\frac{r_{evp} \cdot V_m}{D \cdot A_c} \cdot x\right)} \]

- The larger \( r_{evp} \) (higher heating power), or the smaller cross sectional area \( A_c \),
- The smaller the concentration in the gas \( c_{i,g} \).

- Adding a baffle in the GAr near the top region is expected to help keeping impurities from reaching the LAr surface.

Ref: K. W. Reus et al., Diffusion coefficients in flowing gas. I.
Future work on impurities

- Understand water impurity with more data; all other impurities
- Verification of the baffle idea
- Electron attachment rate
- Electron lifetime
  - vs. impurity concentration
  - vs. E-field
The tool under developing – LArFCS

- Mainly for field response in LArTPCs
- Contains ~250-L LAr
- LAr purity can achieve < 1 ppb level in ~1 week, with continuous gas purification and one time liquid purification in the LAr filling line

- An ideal place for further studying the impurity performances

- Expected cryogenic operation and purity demonstration soon

- More details, please refer to Dr. Yichen Li (yichen@bnl.gov) who is also attending this workshop
Summary

• A mathematical model for impurities in LAr is constructed and validated

• It predicts a way of measuring the Henry’s coefficient for an impurity in argon.  
  - The measured Henry’s coefficient for oxygen is 0.84±0.04, which is consistent with literature;

• It suggests adding a baffle will help in reducing impurity concentrations in the detector.

• More studies are expected to come about with the LArFCS.

Thank you very much!
Backup ...
The full model

(1) Impurity exchange at liquid-gas surface
\[
\frac{dn_{i,g}}{dt} = n_g (c_{i,g}k_{dis} + c_{i,l}k_{dev}) + c_{i,g} \cdot \frac{dn_g}{dt},
\]
\[
\frac{dn_{i,l}}{dt} = -\frac{dn_{i,g}}{dt}.
\]

(2) Evaporation of LAr
\[
\frac{dn_{i,l}}{dt} = -c_{i,l}r_{evp},
\]
\[
\frac{dn_{i,g}}{dt} = -\frac{dn_{i,l}}{dt}.
\]

(3) Purification of LAr in liquid phase
\[
\frac{dn_{i,l}}{dt} = -c_{i,l}r_{cir,l}
\]
\[
\frac{dn_{i,g}}{dt} = 0.
\]

(4) Purification of GAr and its condensation
\[
\frac{dn_{i,l}}{dt} = (1 - \varepsilon_p)c_{i,g}r_{cir,g},
\]
\[
\frac{dn_{i,g}}{dt} = -c_{i,g}r_{cir,g},
\]
\[
r_{cir,g} = r_{evp} = \frac{P_{in}}{\Delta H_{evp}}.
\]

(5) Leakage of impurities from outside source
\[
\frac{dn_{i,l}}{dt} = 0,
\]
\[
\frac{dn_{i,g}}{dt} = r_{lek},
\]

(6) Sampling of Ar
\[
\frac{dn_{i,l}}{dt} = -c_{i,l}r_{sam}(1 + \delta\rho),
\]
\[
\frac{dn_{i,g}}{dt} = c_{i,g}r_{sam}\delta\rho,
\]
\[
\delta\rho = \frac{\rho_g}{\rho_l - \rho_g}.
\]

(7) Outgassing of impurities
\[
\frac{dc_{i,s}}{dt} = c_{i,g}k_{ads}(c_{i,s}^{sat} - c_{i,s}) - k_{out}c_{i,s},
\]
\[
\frac{dn_{i,l}}{dt} = A_{ads}\frac{dc_{i,s}}{dt},
\]
\[
\frac{dn_{i,g}}{dt} = -\frac{dn_{i,l}}{dt},
\]
\[
\frac{dn_{i,l}}{dt} = 0.
\]


- $n_{i,l}, n_{i,g}$: amount of impurity in moles in liquid and gas
- $n_l, n_g$: amount of LAr and GAr in moles
- $c_{i,l}, c_{i,g}$: concentration in liquid and gas, in mole of impurity per mole of argon

- $r_{evp}, r_{cir,g}, r_{cir,l}, r_{lek}, r_{sam}$: rates (in mole/s) for LAr evaporation, GAr circulation, LAr circulation, impurity leakage, LAr sampling
- $r_{evp} = r_{cir,g} = \frac{P_{in}}{\Delta H_{evp}}$, with $P_{in}$ being the total heat (in W) into the LAr, including the heat power leakage, and $\Delta H_{evp} = 161.14/J/g$: LAr heat of vaporization
- $k_{dis}, k_{dev}$: rates (in s$^{-1}$) for dissolution and devolution at the liquid-gas surface
- $k_{dev} = H_{xx}k_{dis}$, with $H_{xx}$ describing the Henry’s coefficient for the impurity in argon
- $k_{ads}, k_{out}$: rates (in s$^{-1}$) for impurity adsorption and outgassing
- $\rho_g, \rho_l$: number density of GAr and LAr
- $\delta\rho \sim 0.005$ for LAr at 90K
- $c_{i,s}$ : impurity concentration on outgassing surface per unit area; $c_{i,s}^{sat}$ : the adsorbed impurity could be saturated
- $\varepsilon_p$ the efficiency of the GAr purifier
The full model

- Summing up all processes, the equations describing the impurity concentrations are expressed in the following:

\[
\frac{dc_{i,l}}{dt} = -\left[ \frac{1}{n_l} \cdot (r_{cir,l} + r_{evp}) + H_{xx}k_{dis} \frac{n_g}{n_l} \right] \cdot c_{i,l} + \frac{1}{n_l} \cdot \left[ k_{dis}n_g + (1 - \epsilon_p)r_{evp} - r_{sam}\delta\rho \right] \cdot c_{i,g},
\]

\[
\frac{dc_{i,g}}{dt} = \frac{1}{n_g} \cdot (n_gH_{xx}k_{dis} + r_{evp} + r_{sam}\delta\rho) \cdot c_{i,l} - \frac{1}{n_g} \cdot \left[ n_gk_{dis} + r_{evp} + A_{ads}k_{ads}(c_{i,s}^{sat} - c_{i,s}) \right] \cdot c_{i,g} + \frac{1}{n_g} \left( r_{lek} + A_{ads}k_{out}c_{i,s} \right),
\]

\[
\frac{dc_{i,s}}{dt} = c_{i,g}k_{ads}(c_{i,s}^{sat} - c_{i,s}) - k_{out}c_{i,s}, \text{ (this equation is from the outgassing process)}
\]

\[
n_l = n_{0,l} - r_{sam} \cdot t \cdot (1 + \delta\rho),
\]

\[
n_g = n_{0,g} + r_{sam} \cdot t \cdot \delta\rho
\]

\[
c_{i,l}(t) = c_{ss,l} + C_1 e^{-k_F t} + C_2 e^{-k_S t},
\]

\[
c_{i,g}(t) = c_{ss,g} + C_3 e^{-k_F t} + C_4 e^{-k_S t}
\]

\[
c_{ss,l} = -\frac{a_{0,l}}{a_5}, \quad \text{The ultimate concentrations} \quad (t \to \infty) \text{ in a LAr detector}
\]

\[
c_{ss,g} = -\frac{a_{0,g}}{a_5},
\]

\[
k_F = \frac{1}{2} \left( a_4 + \sqrt{a_4^2 - 4a_5} \right), \quad \text{Time constants}
\]

\[
k_S = \frac{1}{2} \left( a_4 - \sqrt{a_4^2 - 4a_5} \right),
\]

The coefficients in the solution are

\[
a_4 = \frac{a_1 n_{0,g} + a_2 n_{0,l}}{n_{0,g} n_{0,l}},
\]

\[
a_5 = \frac{a_1 r_{evp} + a_0 r_{cir,l}}{n_{0,g} n_{0,l}},
\]

\[
a_0 = k_{dis} n_{0,g},
\]

\[
a_1 = r_{evp} + r_{cir,l} + H_{xx}k_{dis} n_{0,g},
\]

\[
a_2 = r_{evp} + k_{dis} n_{0,g},
\]

\[
a_3 = r_{evp} + H_{xx}k_{dis} n_{0,g},
\]

\[
a_0,l = \frac{n_{0,l} n_{0,l}}{a_0 n_{lek}},
\]

\[
a_0,g = \frac{a_1 r_{lek}}{n_{0,g} n_{0,l}},
\]

\[
C_1 \text{ to } C_4 \text{ are determined by initial conditions}
\]
ProtoDUNE experience

From Folippo Resnati's talk  https://indico.fnal.gov/event/21535/contribution/4/material/slides/0.pdf

Tests on the purity in ProtoDUNE-SP are compatible with the assumption that most of the impurities come from the vapour:

When stopping the liquid purification, contamination increase slower if the non-purified boil-off is released instead of being re-condensed.

Reducing the liquid argon flow sent to the purification cartridges, the liquid argon bulk purity is not affected in the short time scale of few days, i.e. the recirculation speed is important to reach ultra high purity quickly, and less important to maintain it.

The solubility of a liquid in a gas at low pressures may be calculated from the vapor pressure of the liquid. **Raoult’s law** yields an expression for the mole fraction, $y_1$, of the liquid component in the gaseous phase

$$y_1 = \frac{(1 - x_2) P^*}{P}$$

(1)

where $x_2$ is the mole fraction of the gaseous component dissolved in the liquid, $P^*$ is the vapor pressure of the (pure) liquid, and $P$ is the total pressure.

In the temperature range 25–100°, the solubility in water of argon, nitrogen, and methane is very small, and to a good approximation we may take $\gamma_1^{(P)} = 1$ and $x_2^{(P)} = y_1^{(L)}$ (pure). In the pressure range under consideration here, liquid water is essentially incompressible. The mole fraction of water in the gas may therefore be written

$$y_1 = \frac{(1 - x_2) f_1^{(P)}}{\phi_1 P} \exp \left( \frac{y_1^{(L)} (P - P^*)}{RT} \right)$$

(4)

Since $x_2$ is very small compared to unity, the vapor-phase solubility is determined primarily by the fugacity coefficient $\phi_1$. This may be calculated from the virial equation of state.

$$\ln \phi_1 = \frac{2}{v} (y_{12}B_{13} + y_{13}B_{13}) + \cdots - \ln \left( \frac{P_0}{RT} \right)$$

(5)

**Table I:** Solubility of Water in Compressed Gases

<table>
<thead>
<tr>
<th>$T$, °C</th>
<th>Pressure, atm</th>
<th>$y_1$, exp</th>
<th>$y_1$, cal</th>
<th>$B_{1n}$, ml/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.0</td>
<td>22.20</td>
<td>0.001529</td>
<td>0.001531</td>
<td>$-40 \pm 6$</td>
</tr>
<tr>
<td></td>
<td>30.50</td>
<td>0.001149</td>
<td>0.001149</td>
<td></td>
</tr>
<tr>
<td></td>
<td>38.19</td>
<td>0.000943</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>50.0</td>
<td>0.00621</td>
<td>0.00621</td>
<td>$-28 \pm 5$</td>
</tr>
<tr>
<td></td>
<td>50.0</td>
<td>0.00367</td>
<td>0.00365</td>
<td></td>
</tr>
<tr>
<td></td>
<td>59.04</td>
<td>0.00242</td>
<td>0.00242</td>
<td></td>
</tr>
<tr>
<td></td>
<td>75.89</td>
<td>0.001956</td>
<td>0.001957</td>
<td></td>
</tr>
<tr>
<td></td>
<td>75.0</td>
<td>0.01009</td>
<td>0.01066</td>
<td>$-20 \pm 4$</td>
</tr>
<tr>
<td></td>
<td>60.35</td>
<td>0.00721</td>
<td>0.00723</td>
<td></td>
</tr>
<tr>
<td></td>
<td>88.55</td>
<td>0.00523</td>
<td>0.00522</td>
<td></td>
</tr>
<tr>
<td>100.0</td>
<td>56.42</td>
<td>0.01994</td>
<td>0.01995</td>
<td>$-15.5 \pm 3$</td>
</tr>
<tr>
<td></td>
<td>78.44</td>
<td>0.01503</td>
<td>0.01491</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100.19</td>
<td>0.01218</td>
<td>0.01219</td>
<td></td>
</tr>
</tbody>
</table>

**Nitrogen**

**Argon**
Henry’s law

At a constant \( T \), the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid.

An equivalent way of stating the law: the solubility (\( C \), unit in mL/L e.g.) of a gas in a liquid is proportional to the partial pressure (unit in atm e.g.) of the gas above the liquid:

\[
C = kP_{gas}
\]

**Henry solubility** \( H^{CP} \) \( \equiv \frac{c_a}{p} \) with \( c_a \) the concentration of a species in liquid and \( p \) the partial pressure of that species in gas phase. The SI unit for \( H^{CP} \) is \( \text{mol m}^{-3} \text{Pa} \) or often used as \( \text{mol L}^{-1} \text{atm} \).

\( H^{CP} \) can be expressed as the dimensionless ratio between \( c_a \) and \( c_g \), the concentration in gas phase:

\[
H^{CC} \equiv \frac{c_a}{c_g}
\]

And \( H^{CC} = H^{CP} \cdot RT \) for ideal gas with \( R, T \) the gas constant and temperature.

Another Henry’s law solubility constant is \( H^{XP} \equiv \frac{x}{p} \) with \( x \) the molar mixing ratio in the liquid. The conversion between \( x \) and \( c_a \) is \( c_a \approx x \cdot \frac{\rho_L}{M_L} \), \( \rho, M \) are density and molar mass of the liquid. Therefore \( H^{XP} = \frac{M_L}{\rho_L} \cdot H^{CP} \). \( H^{XP} \) has an SI unit of \( Pa^{-1} \).

Henry solubility defined via molality: \( H^{BP} \equiv \frac{b}{p} \) with \( b \) representing molality (of the solved species in liquid). \( H^{BP} \) has SI unit of \( \text{mol} \cdot \text{kg}^{-1} \cdot Pa^{-1} \). If there is only one solute in the solvent, \( b \) can be related with \( c_a \) by \( c_a = b\rho_L/(1 + bM_L) \approx b\rho_L \) (approximation is valid at very small concentration), thus \( H^{BP} = H^{CP}/\rho_L \).

**Henry volatility** is defined as \( K_{H}^{PC} = \frac{p}{c_a} = 1/H^{CP} \); similarly there are other definitions of volatility terms, I ignore them here.

The Henry’s coefficient we refer to \( K_h = c_g/c_a \) (volatility term)
Figure 1: Drift electron attenuation as a function of maximum field of 0.273 kV/cm. The colored curves correspond to different electron drift-lifetime ($\tau$). In 100% pure liquid argon, the infinite lifetime.

One of the important operational requirements of a LAr detector such as oxygen and water at extremely low concentrations. Drifting ionization electrons (signal) and thereby reduce the sensitivity of energy measurements and track reconstruction. The electron lifetime is inversely proportion to the drift distance of 2.56 cm (equivalent to a 5-ms lifetime in an electric field of 0.273 kV/cm), the O$_2$ equivalent contamination is required to be as low as 60 parts per trillion (ppt). Similarly, to achieve a signal loss of less than 20% (or a lifetime of 10 ms at 0.273 kV/cm), the O$_2$ equivalent concentration is required to be less than 30 ppt. Commercial liquid argon typically contains parts per million (ppm) oxygen concentration levels. Liquid argon can also become contaminated inside the cryostat due to the out-gassing of the warm walls, cables and other TPC components present in the gaseous argon volume. Additionally, virtual leaks (such as from the parts located close to the feedthroughs) can also become a constant source of impurities. The desired purity is therefore achieved using a continuous liquid-argon recirculation system.

Fig. 9. Electron lifetime $\tau$ measured in LAr doped with 3 ppb of O$_2$. The O$_2$ was introduced into the cell after it had been half filled with purified Ar. The jumps in $\tau$ are due to stirring (lasting between 20 to 60 min). The measurement was stopped when there was no more change in $\tau$ after stirring.
Figure 3. Liquid-sampling valve.