An impurity model for LAr detectors

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BROOKHAVEN
NATIONAL LABORATORY

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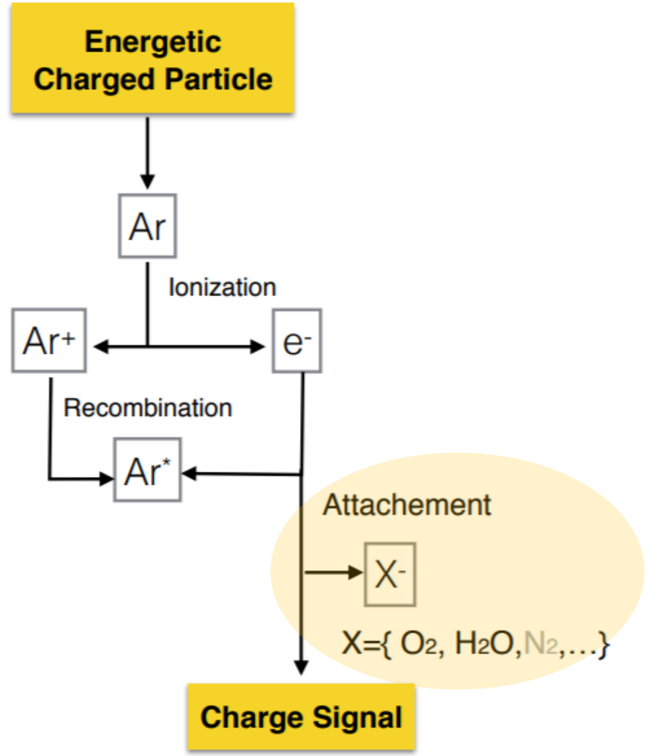
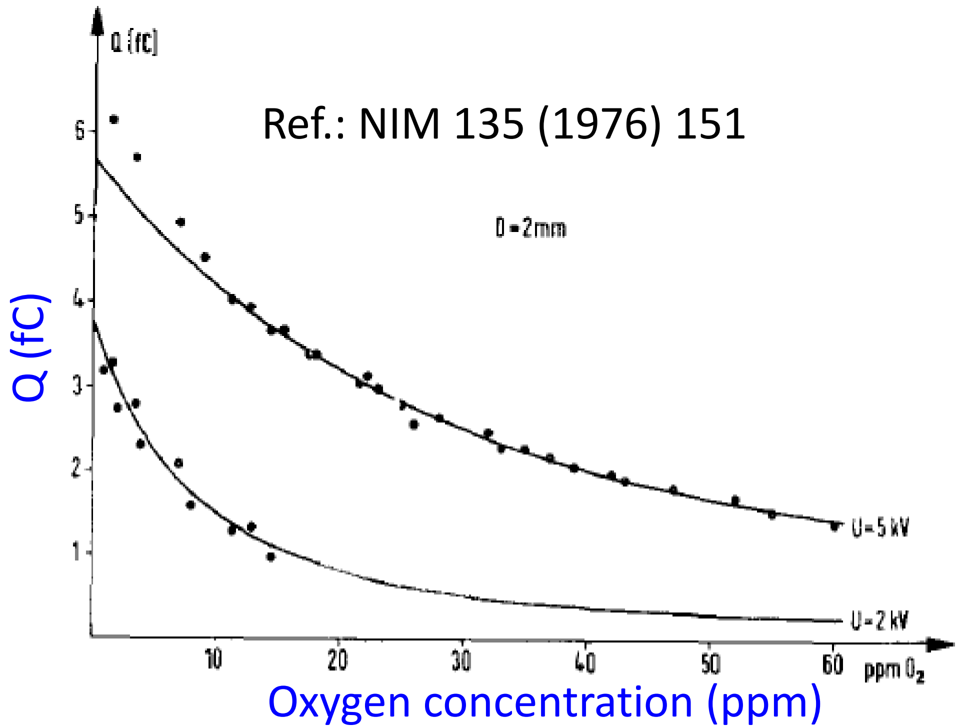
Outline

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

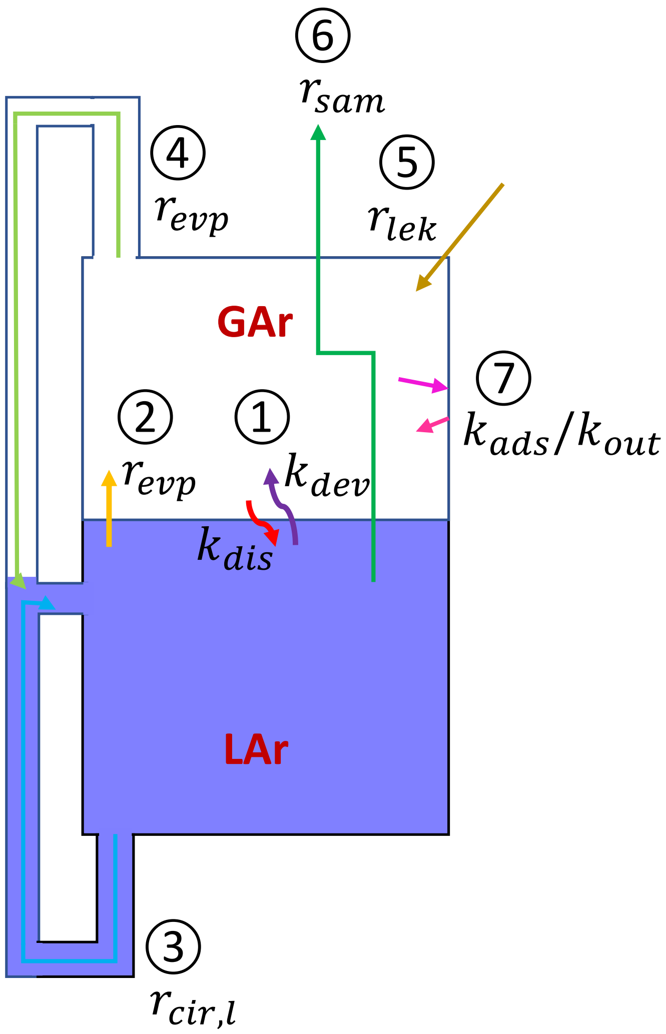
Motivation

- 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

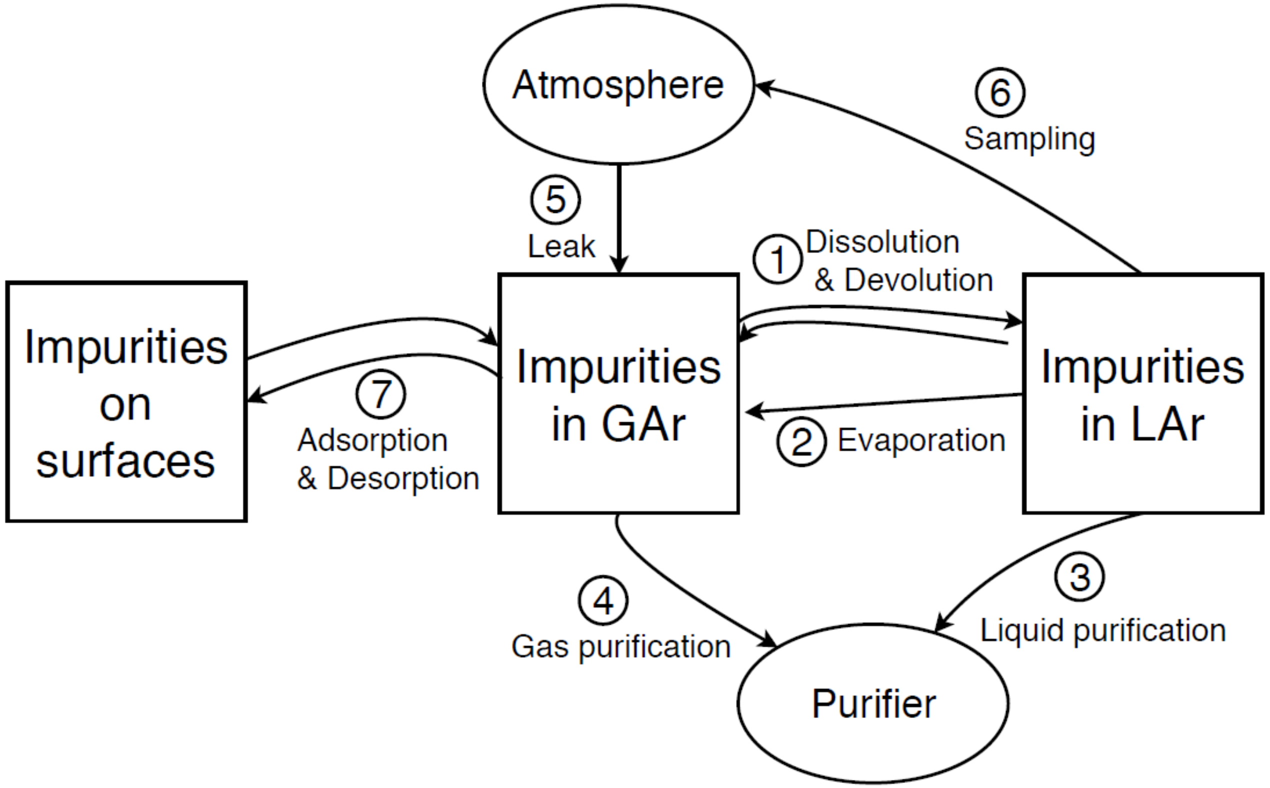



Ref.: NIM 135 (1976) 151

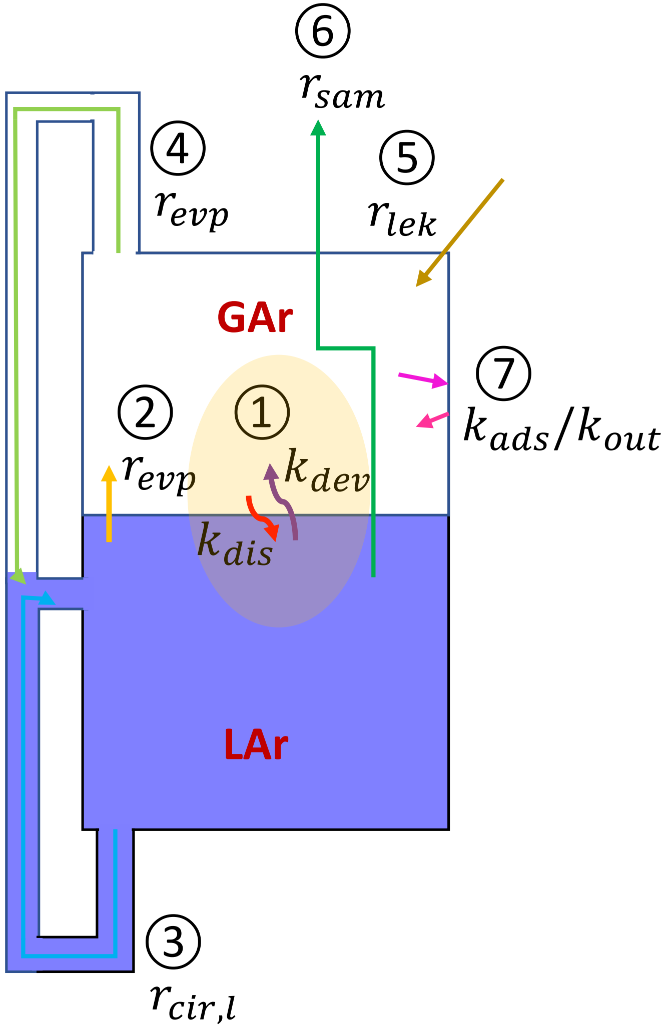
Model description – overview



Seven processes are considered for the impurity dynamics



Model description – overview



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

$$\frac{dn_{i,g}}{dt} = n_g(-c_{i,g}k_{dis} + c_{i,l}k_{dev}) + c_{i,g} \cdot \frac{dn_g}{dt},$$
$$\frac{dn_{i,l}}{dt} = -\frac{dn_{i,g}}{dt}$$

$n_{i,l}, n_{i,g}$: 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)

$c_{ss,l}, c_{ss,g}, k_F, k_S$ are functions of the model parameters

- Analyzing k_S:

$$H = \frac{Cleaning\ rate\ of\ argon}{Evaporation\ rate\ of\ argon}$$

Heating power to the LAr

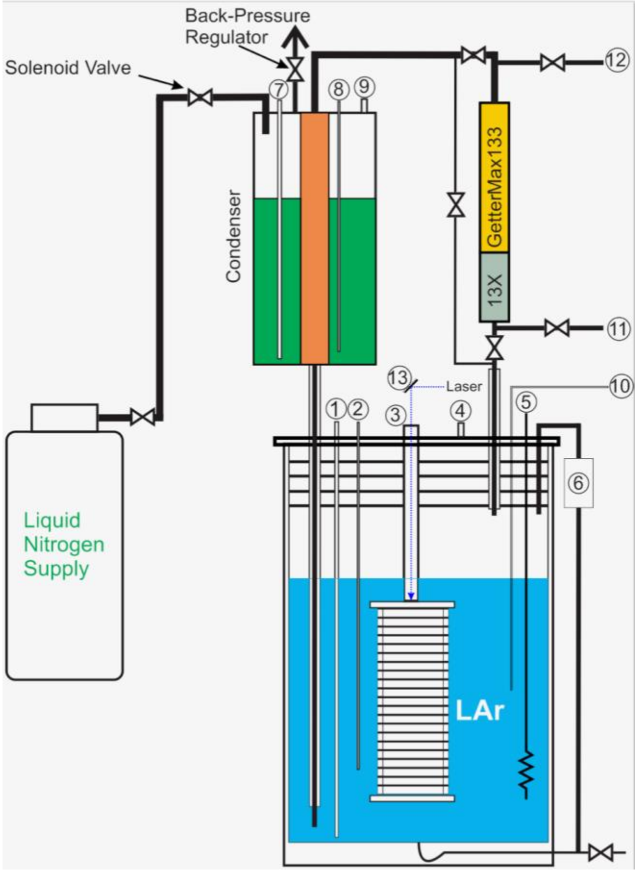
$$H \equiv \frac{c_{ss,g}}{c_{ss,l}}$$

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

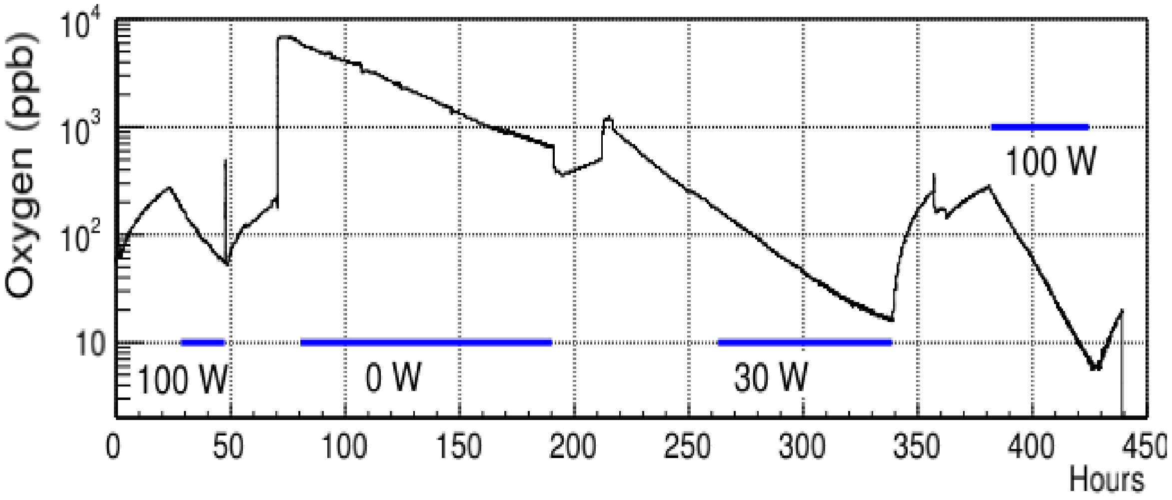
- For studying basic properties of LAr: measured longitudinal diffusion of electrons (NIMA 816 (2016) 160)
- Gas purification only
- Additional heating power can be varied 0-150 W
- Oxygen and water concentrations measured by sampling LAr into gas analyzers (0.2 ppb precision)



Details: JINST 16 06 t06001

Henry's coefficient for oxygen (H_{Oxygen})

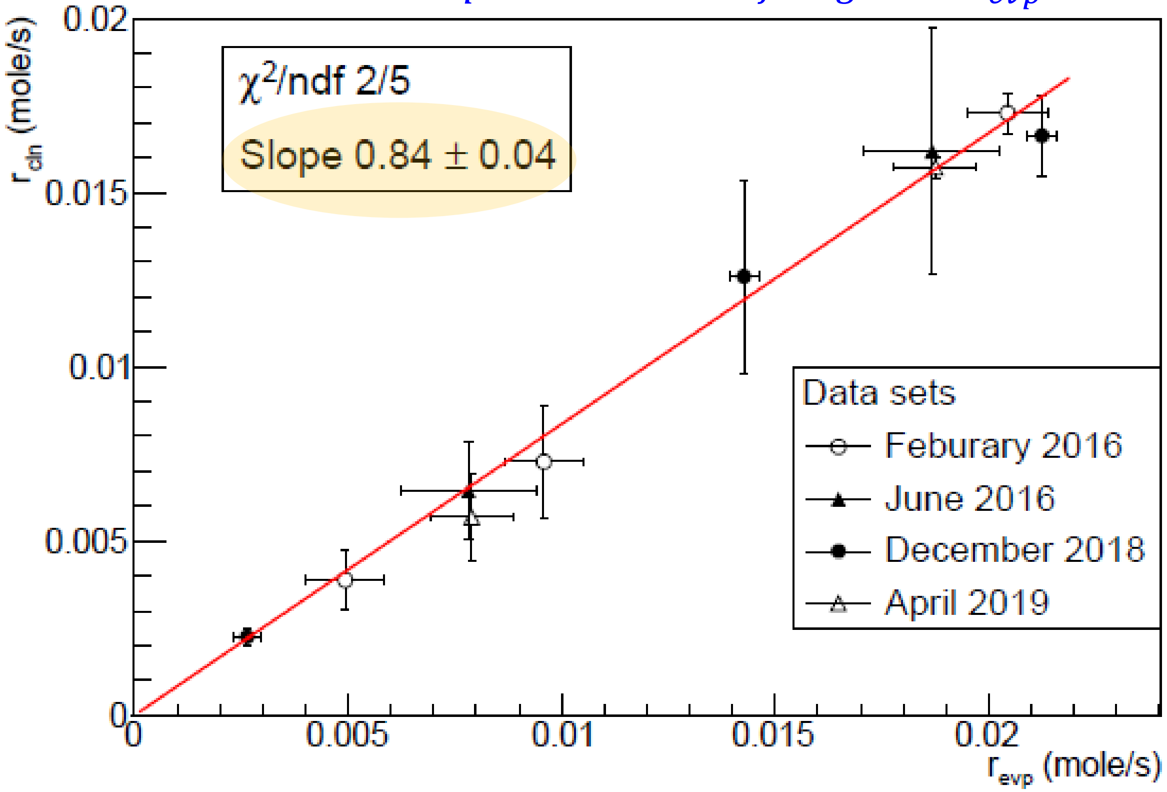
- Data used for analysis selected based on slow control data (LAr level, heater temperature, etc.)



Oxygen concentration data (Feb. 2016 data set)

- Cleaning rates measured at different heating powers

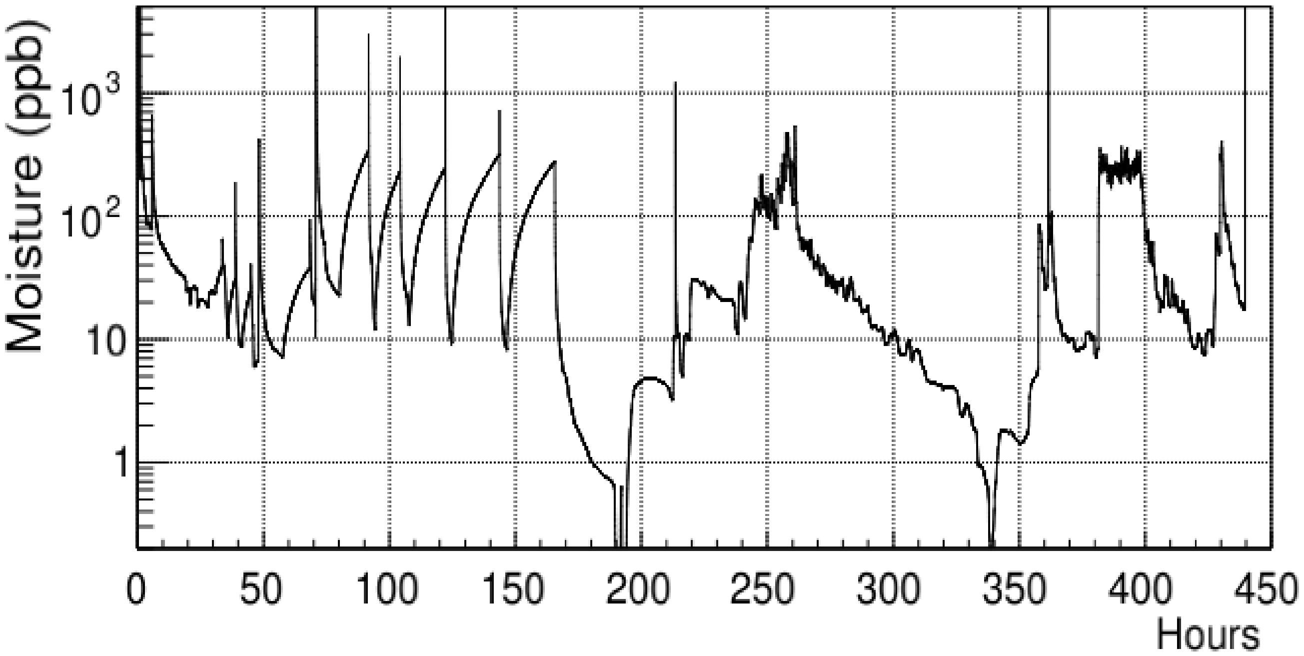
$$H = \frac{Cleaning\ rate\ of\ argon}{Evaporation\ rate\ of\ argon} = \frac{r_{cln}}{r_{evp}}$$



- $H_{Oxygen} = 0.84 \pm 0.04$, 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



Water concentration data (Feb. 2016 data set)

$H_{water} = 3 \times 10^{-9}$ from NIST REFPROP

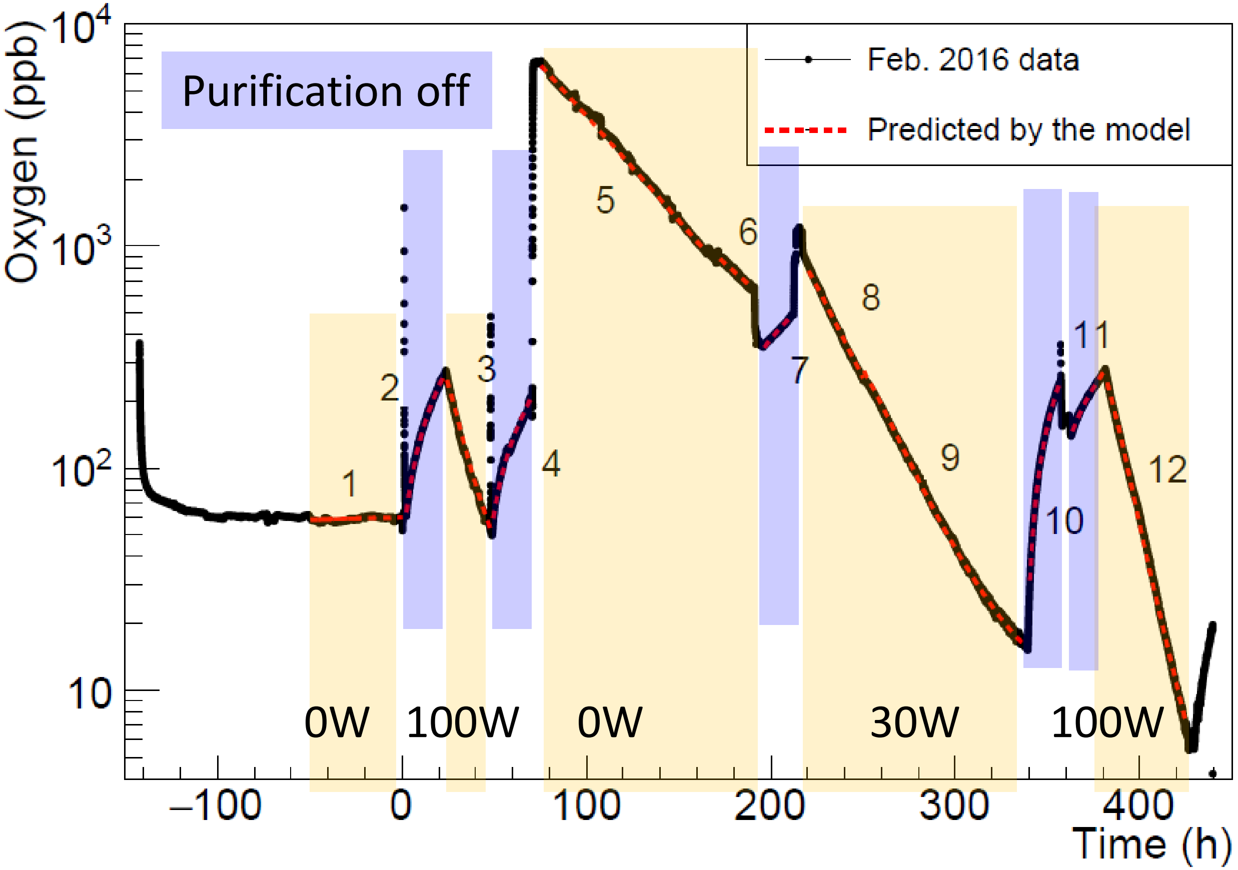
- from equation of state calculation
- Water vapor pressure ~10^{-22} bar (at 90 K)

(extracted from empirical equations)

- More data are needed

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:

- ~ 5×10^{-6} mole/h with purification off;

- ~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

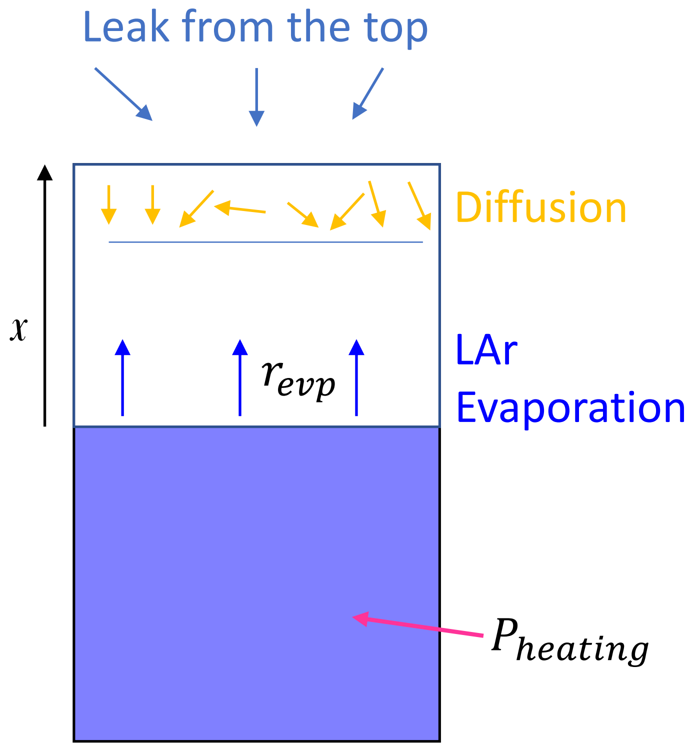
- The dependence of leak rate on the input heating power can be explained by a simple diffusion model:

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

r_{evp} the evaporation rate
V_m the mole volume of GAr,
A_c the cross sectional area perpendicular to the flow direction
D the diffusion coefficient of the impurity

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

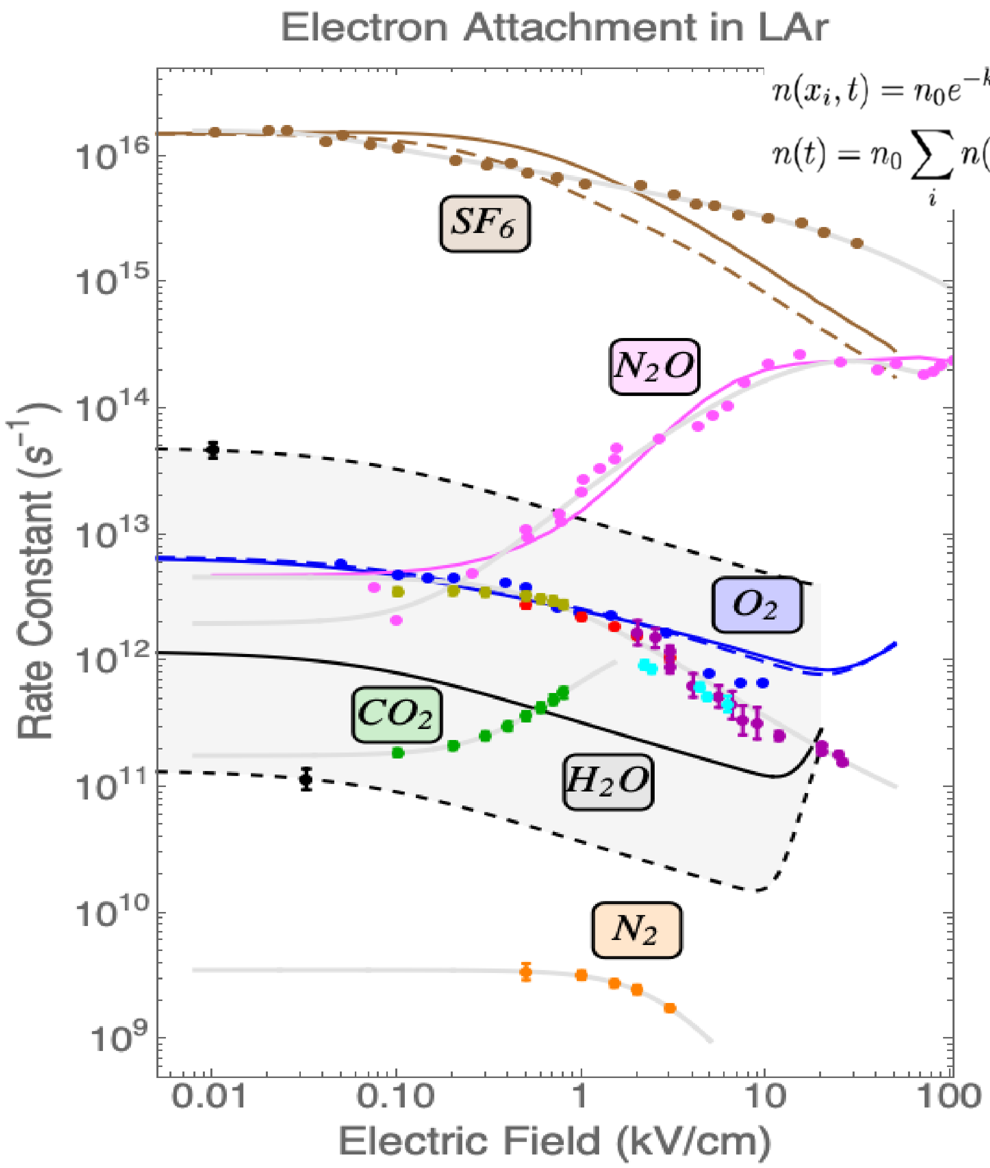
- Adding a baffle in the GAr near the top region is expected to help keeping impurities from reaching the LAr surface.



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



$n(x_i, t) = n_0 e^{-k_A x_i t}$ for mole fraction x_i of impurity i

$n(t) = n_0 \sum_i n(x_i, t)$ for all impurities

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

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(1) Impurity exchange at liquid-gas surface

$$\frac{dn_{i,g}}{dt} = n_g\left(-c_{i,g}k_{dis} + c_{i,l}k_{dev}\right) + c_{i,g}\cdot\frac{dn_g}{dt},$$

$$\frac{dn_{i,l}}{dt} = -\frac{dn_{i,g}}{dt}$$

(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

$$\frac{dn_{i,l}}{dt} = (1-\epsilon_P)c_{i,g}r_{cir,g},$$

$$\frac{dn_{i,g}}{dt} = -c_{i,g}r_{cir,g},$$

$$r_{cir,g} = r_{evp} = \frac{P_{in}}{\Delta H_{evp}}$$

(5) Leakage of impurities from outside source

$$\frac{dn_{i,l}}{dt} = 0,$$

$$\frac{dn_{i,g}}{dt} = r_{lek},$$

(6) Sampling of Ar

$$\frac{dn_{i,l}}{dt} = -c_{i,l}r_{sam}(1+\delta\rho),$$

$$\frac{dn_{i,g}}{dt} = c_{i,l}r_{sam}\delta\rho,$$

$$\delta\rho = \frac{\rho_g}{\rho_l-\rho_g}$$

(7) Outgassing of impurities

$$\frac{dc_{i,s}}{dt} = c_{i,g}k_{ads}\left(c_{i,s}^{sat} - c_{i,s}\right) - k_{out}c_{i,s},$$

$$\frac{dn_{i,s}}{dt} = A_{ads}\frac{dc_{i,s}}{dt},$$

$$\frac{dn_{i,g}}{dt} = -\frac{dn_{i,s}}{dt},$$

$$\frac{dn_{i,l}}{dt} = 0$$

Ref. for (1): G. M. Nathanson et. al., “Dynamics and Kinetics at the Gas-Liquid Interface”, J. Phys. Chem., 100(31):13007-13020, 1996.

Ref. for (7): J. Zhang, “Physical insights into kinetic models of adsorption”, Separation and Purification Technology, 229:115832, 2019.

- $n_{i,l}, n_{i,g}$: 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

$$n_{i,l} = c_{i,l}n_l,$$
$$n_{i,g} = c_{i,g}n_g$$

- $r_{evp}, r_{cir,g}, r_{cir,l}, r_{lek}, r_{sam}$: 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
- ρ_g, ρ_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
- ϵ_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

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

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

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

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

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

$$\boxed{\begin{aligned} c_{i,l}(t) &= c_{ss,l} + C_1 e^{-k_F t} + C_2 e^{-k_S t}, \\ c_{i,g}(t) &= c_{ss,g} + C_3 e^{-k_F t} + C_4 e^{-k_S t} \end{aligned}}$$

$$\left.\begin{aligned} c_{ss,l} &= -\frac{a_{0,l}}{a_5}, \\ c_{ss,g} &= -\frac{a_{0,g}}{a_5}, \end{aligned}\right\}$$

The ultimate concentrations ($t \rightarrow \infty$) in a LAr detector

$$\left.\begin{aligned} k_F &= \frac{1}{2}\left(a_4 + \sqrt{a_4^2 - 4a_5}\right), \\ k_S &= \frac{1}{2}\left(a_4 - \sqrt{a_4^2 - 4a_5}\right), \end{aligned}\right\}$$

Time constants

The coefficients in the solution are

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

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

$$a_{0,l} = \frac{a_0 r_{lek}}{n_{0,g}n_{0,l}},$$

$$a_{0,g} = \frac{a_1 r_{lek}}{n_{0,g}n_{0,l}},$$

$$a_0 = k_{dis}n_{0,g},$$

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

$$a_2 = r_{evp} + k_{dis}n_{0,g},$$

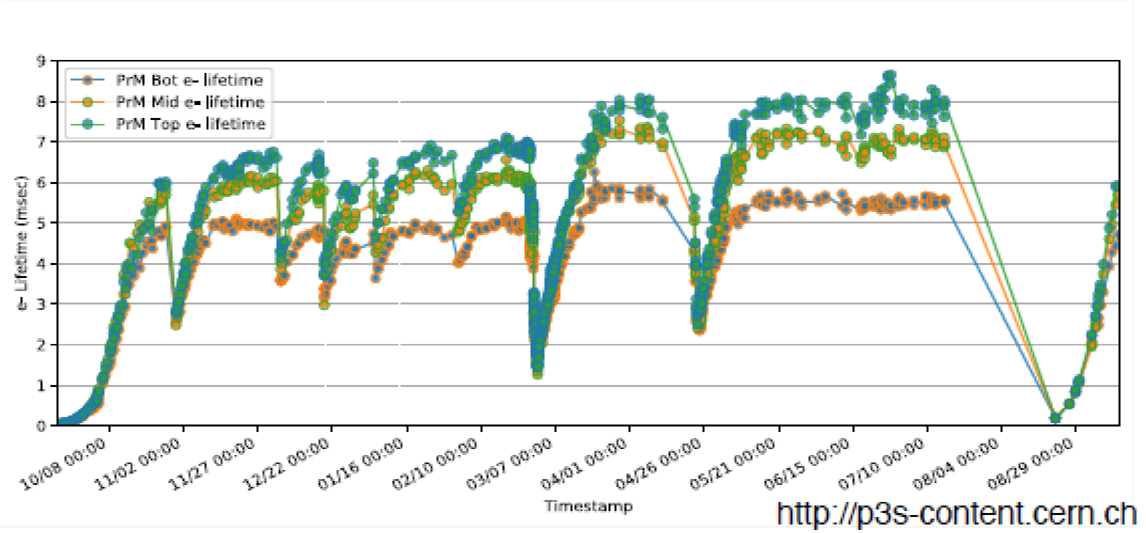
$$a_3 = r_{evp} + H_{xx}k_{dis}n_{0,g}.$$

C_1 to C_4 are determined by initial conditions

ProtoDUNEs experience

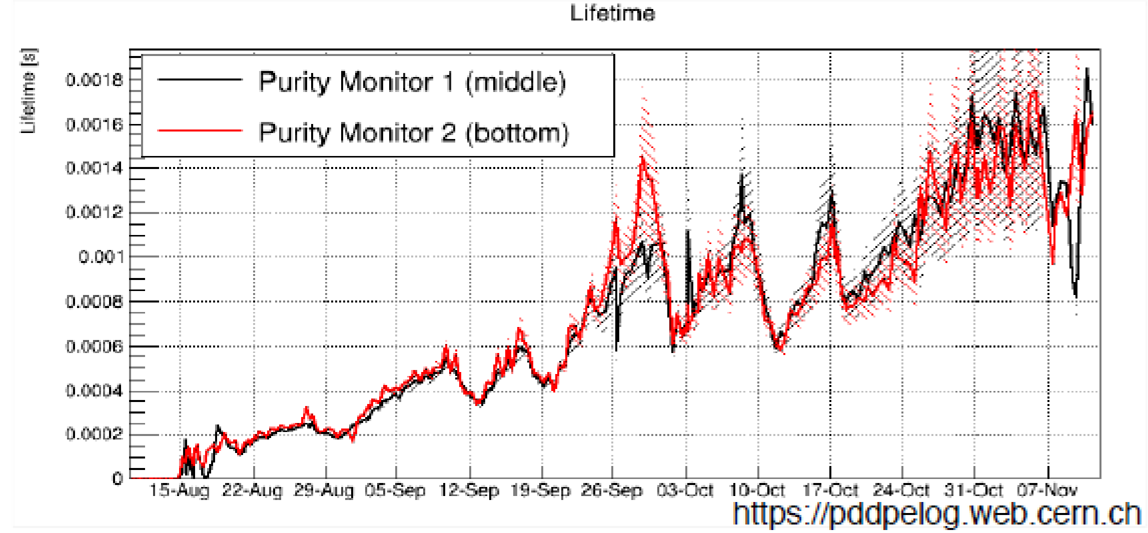
From Folippo Resnati’s talk https://indico.fnal.gov/event/21535/contribution/4/material/slides/0.pdf

NP04



http://p3s-content.cern.ch

NP02

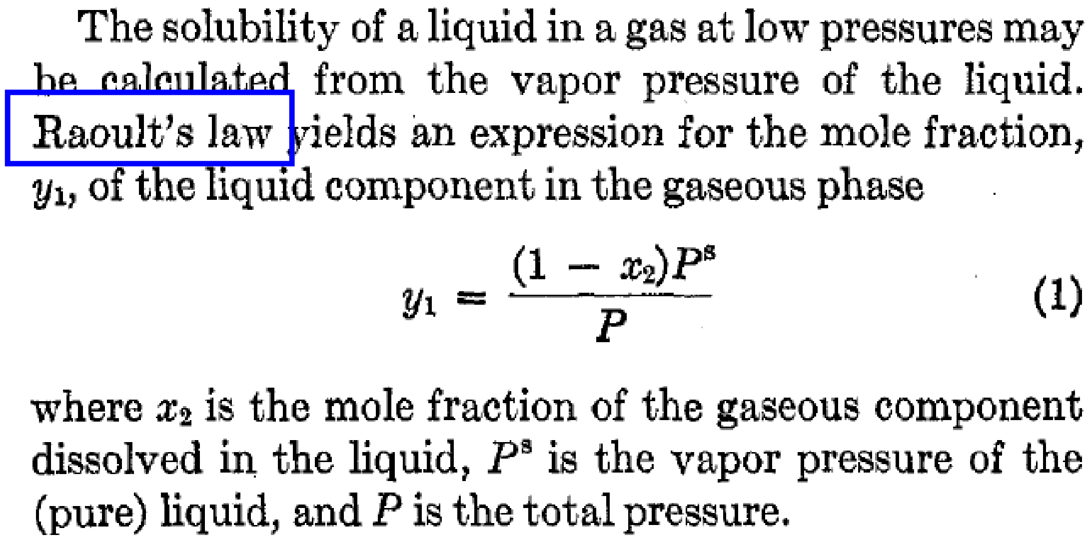


https://pddpelog.web.cern.ch

Tests on the purity in ProtoDUNE-SP are compatible with the assumption that most of the impunities comes 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.

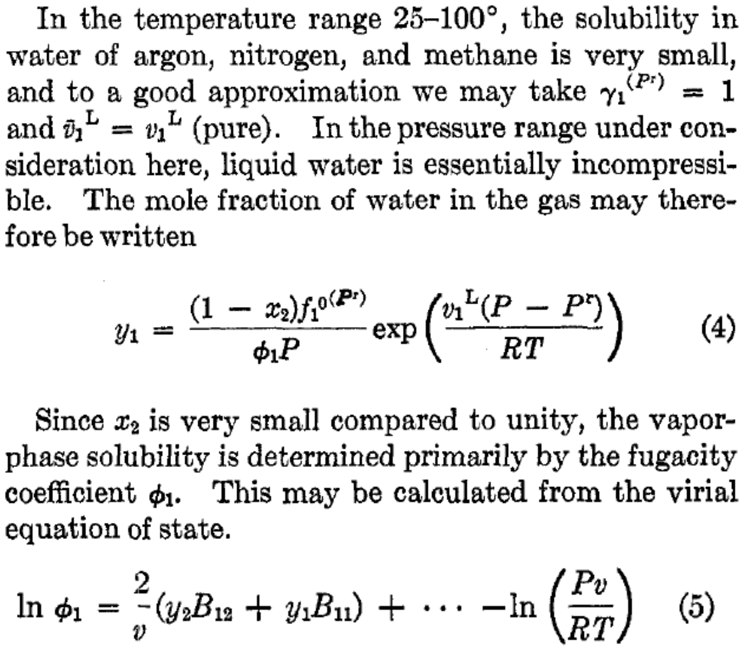
Ref: "Solubility of Water in Compressed Nitrogen, Argon, and Methane" by M. Rigby and J. M. Prausnitz, Journal of Physical Chemistry, Vol 72 (1), 1968.



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

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

where x_2 is the mole fraction of the gaseous component dissolved in the liquid, P^s 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 $\gamma_1^{(P^r)} = 1$ and $\bar{v}_1^L = v_1^L$ (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

$$y_1 = \frac{(1 - x_2)f_1^{0(P^r)}}{\phi_1 P} \exp\left(\frac{v_1^L(P - P^r)}{RT}\right) \qquad (4)$$

Since x_2 is very small compared to unity, the vapor-phase solubility is determined primarily by the fugacity coefficient ϕ_1. This may be calculated from the virial equation of state.

$$\ln \phi_1 = \frac{2}{v}(y_2B_{12} + y_1B_{11}) + \cdots - \ln\left(\frac{Pv}{RT}\right) \qquad (5)$$

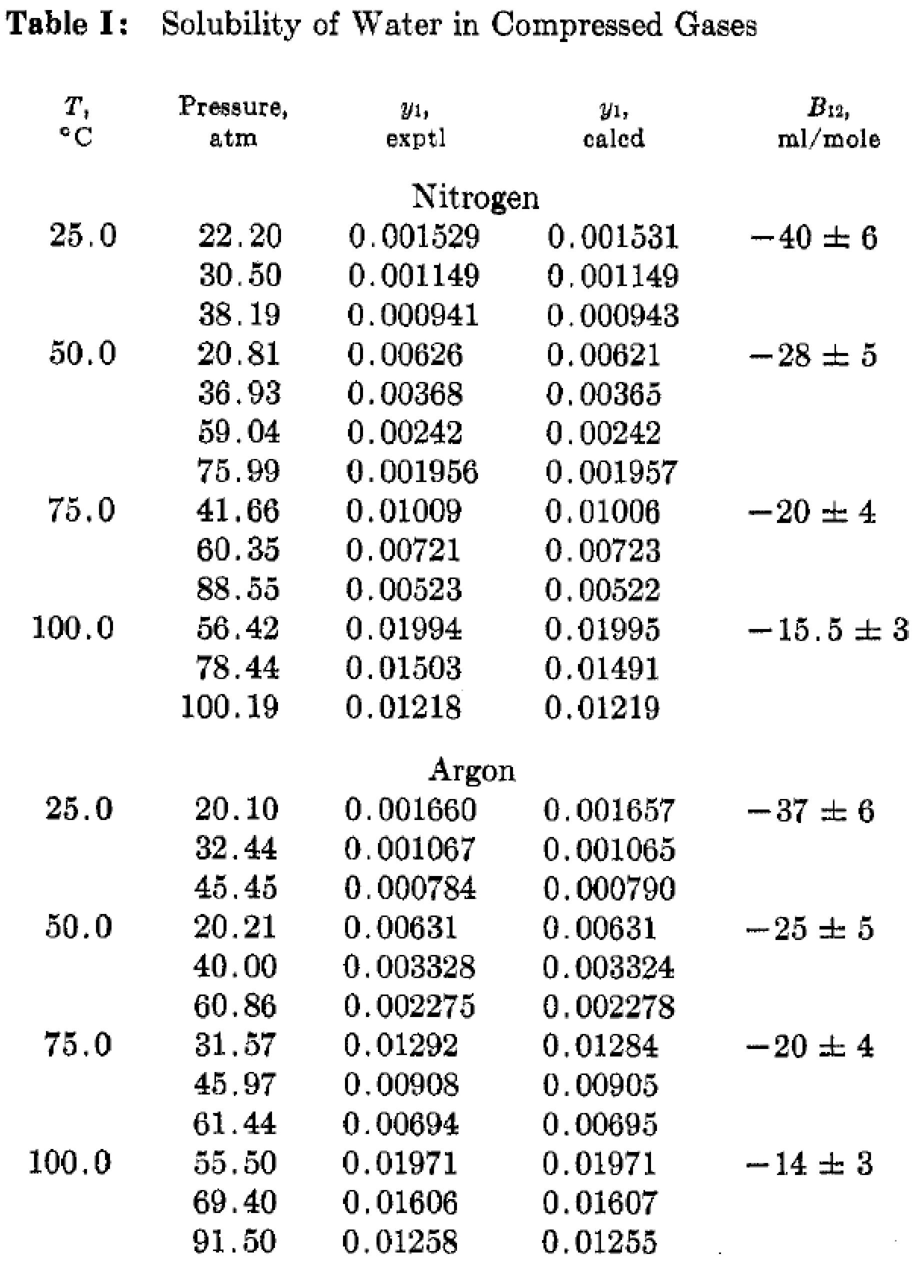


Table I: Solubility of Water in Compressed Gases

T, °C	Pressure, atm	y_1, exptl	y_1, calcd	B_{12}, ml/mole
		Nitrogen		
25.0	22.20	0.001529	0.001531	−40 ± 6
	30.50	0.001149	0.001149	
	38.19	0.000941	0.000943	
50.0	20.81	0.00626	0.00621	−28 ± 5
	36.93	0.00368	0.00365	
	59.04	0.00242	0.00242	
	75.99	0.001956	0.001957	
75.0	41.66	0.01009	0.01006	−20 ± 4
	60.35	0.00721	0.00723	
	88.55	0.00523	0.00522	
100.0	56.42	0.01994	0.01995	−15.5 ± 3
	78.44	0.01503	0.01491	
	100.19	0.01218	0.01219	
		Argon		
25.0	20.10	0.001660	0.001657	−37 ± 6
	32.44	0.001067	0.001065	
	45.45	0.000784	0.000790	
50.0	20.21	0.00631	0.00631	−25 ± 5
	40.00	0.003328	0.003324	
	60.86	0.002275	0.002278	
75.0	31.57	0.01292	0.01284	−20 ± 4
	45.97	0.00908	0.00905	
	61.44	0.00694	0.00695	
100.0	55.50	0.01971	0.01971	−14 ± 3
	69.40	0.01606	0.01607	
	91.50	0.01258	0.01255	

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:

$$\mathrm{C} = kP_{gas}$$

Henry **solubility** $H^{CP} \equiv c_a/p$ 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 $\frac{mol}{m^3 Pa}$ or often used as $\frac{mol}{L\cdot atm}$.

H^{CP} can be expressed as the dimensionless ratio between c_a and c_g, the concentration in gas phase:
$H^{CC} \equiv c_a/c_g$
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 $H^{xP} \equiv x/p$ with x the molar mixing ratio in the liquid. The conversion between x and c_a is $c_a \approx x \cdot \rho_L/M_L$, ρ, M are density and molar mass of the liquid. Therefore $H^{xP} = \frac{\mathrm{M_L}}{\mathrm{\rho}_L} \cdot H^{CP}$. H^{xP} has an SI unit of Pa^{-1}.

Henry solubility defined via molality: $H^{bP} \equiv b/p$ with b representing molality (of the solved species in liquid). H^{bP} has SI unit of $mol \cdot kg^{-1} \cdot Pa^{-1}$. 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 $\mathrm{K_H} = c_g/c_a$ (volatility term)

Ref: Atmos. Chem. Phys., 15, 4399-4981, 2015,
R. Sander, "Compilation of Henry's law constants for water as solvent"

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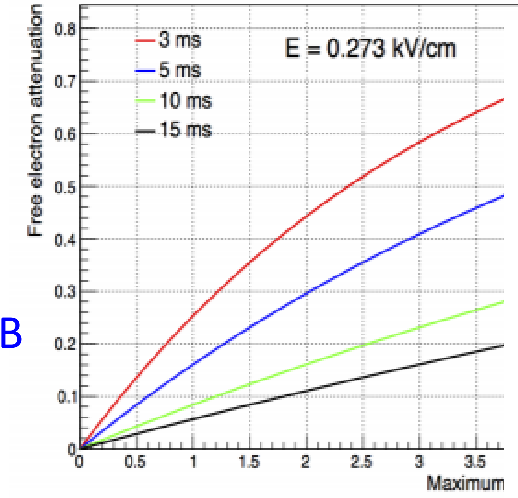

Figure 1: Drift electron attenuation as a function of maxi field of 0.273 kV/cm. The colored curves correspond to diffe electron drift-lifetime (τ). In 100% pure liquid argon, el infinite lifetime.

One of the important operational requirements of a LAr' ties such as oxygen and water at extremely low concentrati drifting ionization electrons (signal) and thereby reduce the can affect both energy measurements and track reconstructi anode wires. The electron lifetime is inversely proportiona and hence provides a direct measurement of the liquid arg Figure 1 shows the drift-electron attenuation as a function of maximum drift path for an uniform electric field of 0.273 kV/cm and a drift velocity of 114 cm/ms for different electron drift-lifetimes. To achieve less than 36% signal loss for a drift distance of 2.56 m (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

NIMA 305 (1991) 177

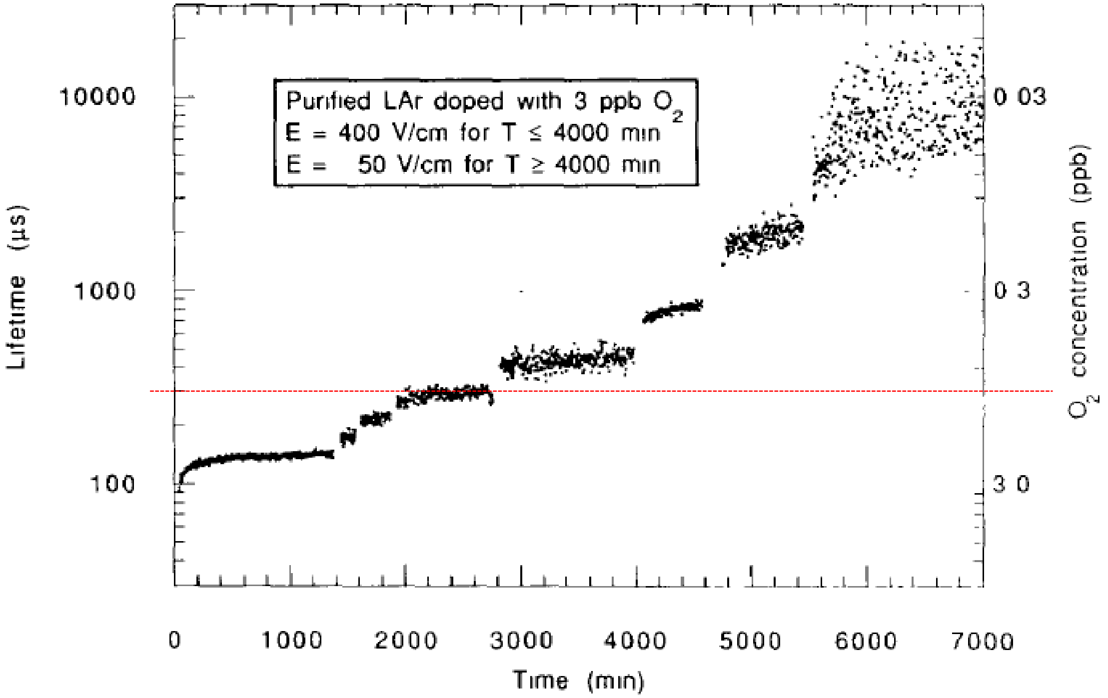

Fig. 9. Electron lifetime τ measured in LAr doped with 3 ppb of O_2. The O_2 was introduced into the cell after it had been half filled with purified Ar. The jumps in τ are due to stirring (lasting between 20 to 60 min). The measurement was stopped when there was no more change in τ after stirring.

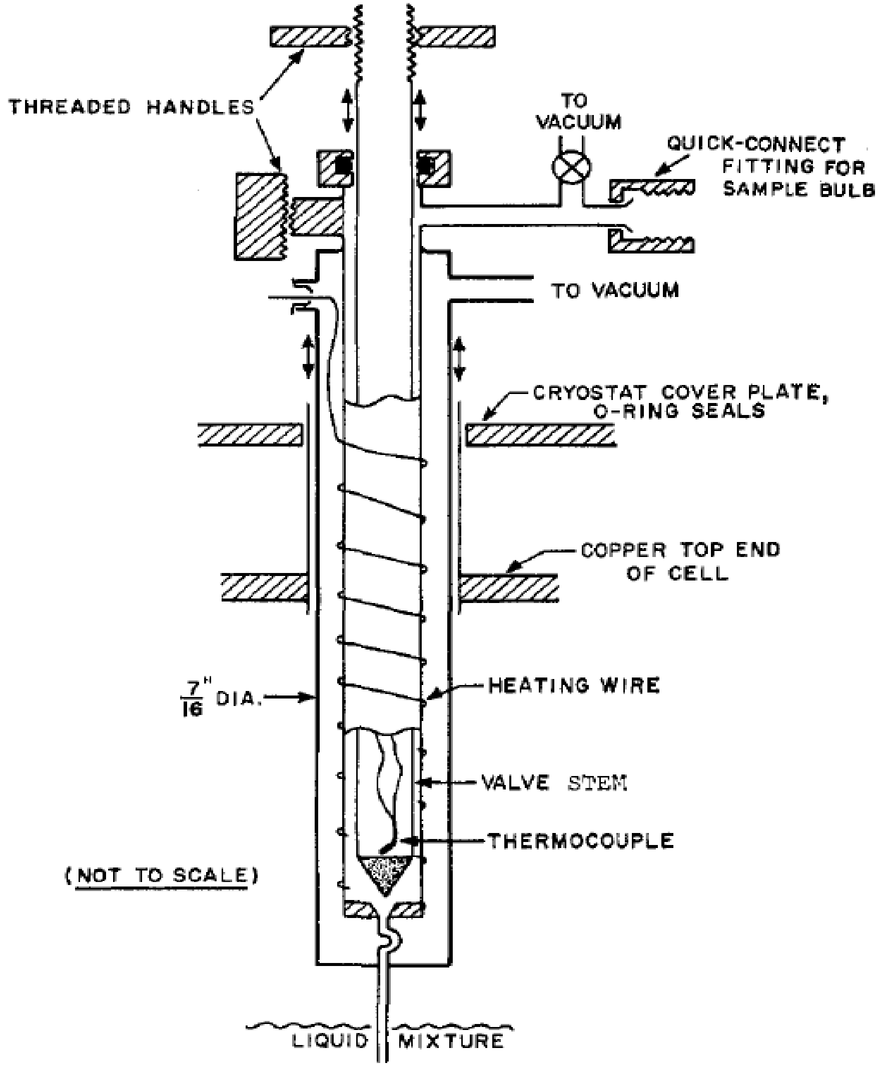

Figure 3. Liquid-sampling valve.

Ref: G. T. Preston et. al., “Solubilities of hydrocarbons and carbon dioxide in liquid methane and in liquid argon”, J Phys. Chem., 75(15):2345, 1971