What we (yet) want to know about impurities in LAr

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What we want to know
Question #1

The most important (useful) question is:

What is the electron attachment to H_2O in LAr?

What we want to know
Questions #2

If the attachment coefficient for water is large, then we need to understand how to minimize its presence in LAr.

The important questions (all at 90K) are:

1. What is the solubility limit of H_2O in LAr?
2. What is the adsorption isotherm for H_2O on stainless steel?
3. Ditto for the adsorption/absorption of H_2O on/in plastics?
4. What is Henry's constant for H_2O in LAr?
5. What construction materials introduce the least (most) H_2O into the detector?

What we want to know
Questions #3

Independent of the relative importance of H_2O, we would like to determine:

1. Are there impurities other than O_2, H_2O, and N_2 in *commercial* LAr that limit the electron lifetime?
   a) Measure lifetime and O_2, H_2O, and N_2 concentrations, all simultaneously.
   b) Compute the lifetime from simultaneously measured concentrations and the known attachment coefficients.
   c) Compare a) and b); if they are significantly different, there are unknown impurities – find them.
2. Same questions for *purified* LAr with common construction materials immersed in it. Find any additional impurities from materials of construction that limit lifetime.

What we want to know
Questions #4

We believe, based on results shown in our purity paper, that a baffle might reduce the effective source of impurities into LAr.

1. Can we verify this ?
   a) What is the reduction in the true leak rate by the natural laminar flow from evaporation at the LAr surface (no baffle)?
   b) Can this reduction be maximized by adjusting operational parameters?
   c) Can an added baffle reduce this rate further?
2. What are the optimal parameters of such a baffle?

What we want to know
Questions #5

What about nitrogen, which is not removed by the combination of the copper getter and molecular sieve purifier at low temperature? It will accumulate in the LAr over time, and will eventually reduce the electron lifetime and the scintillation light yield.

We can estimate this from our data with the Small Test Stand.

a) The oxygen leak rate (no purification) was measured to be 1.7×10^{-9} mol/s.
b) The source of oxygen and nitrogen is air, which is 22% O_2 and 78% N_2.
c) The cryostat contains 700 mol of argon.
d) The rate of N_2 accumulation is $78/21 \times 1.7 \times 10^{-9} \times 10^{6} / 700$ ppm/s = 0.7 ppm/day

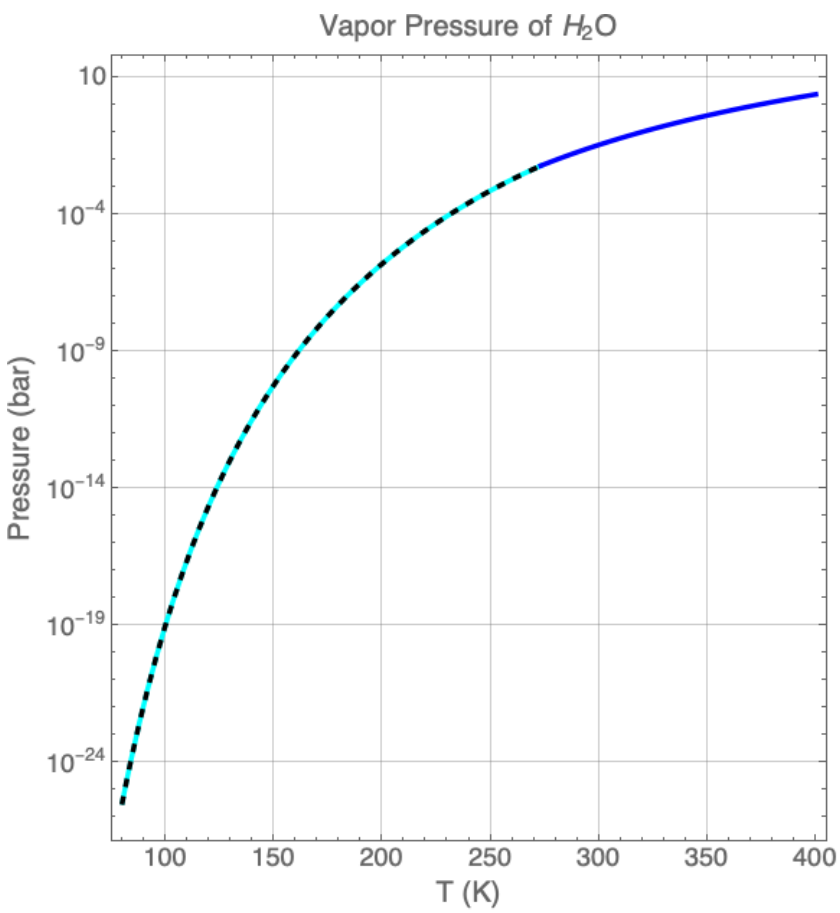
Our system accumulates N_2 at the rate of 0.7 ppm per day. This produces an electron lifetime of 0.4 ms after one day.

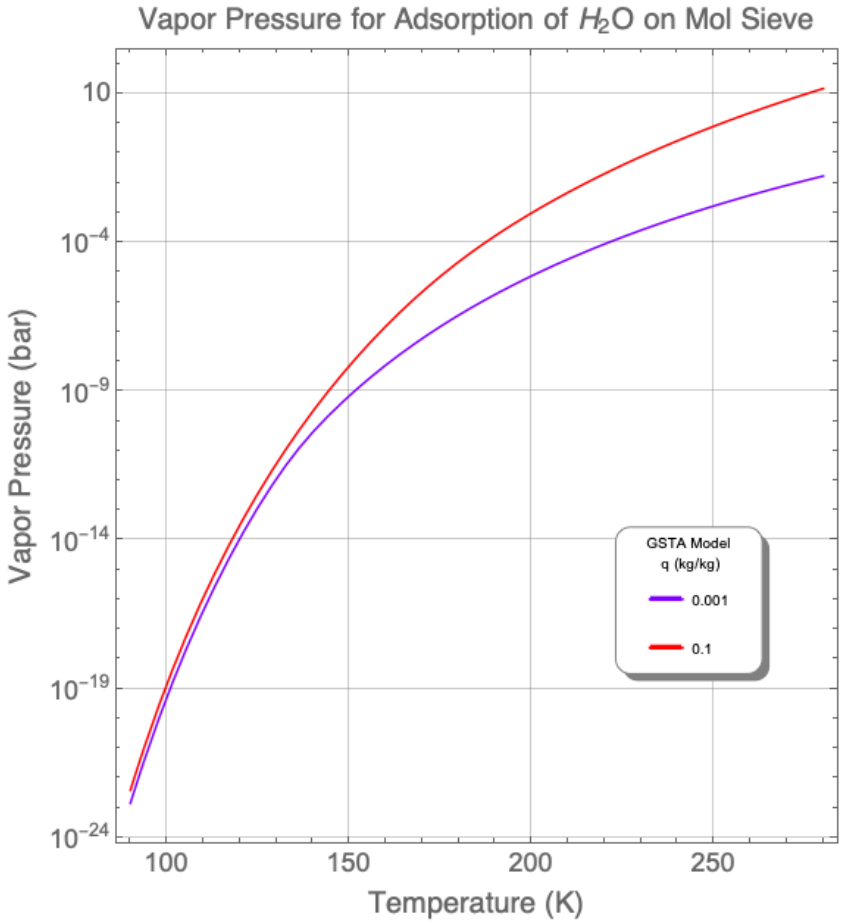
The Problem of Water in LAr

Vapor Pressure of H_2O

At 90K the vapor pressure of water ice is $1.39\ 10^{-22}$ bar, or 3.7 molecules/liter gas

The GSTA model fits for 13X imply a similar low vapor pressure at low temperatures.





1. W. Wagner, et al., J. Phys. Chem. Ref. Data 40 (2011) 043103.
2. N. Fray and B. Schmitt, Planetary and Space Science 57 (2009) 2053.

Desorption Rate Constants: Temperature Dependence

Water desorption by stainless steel and FR4

Water Desorption by FR4

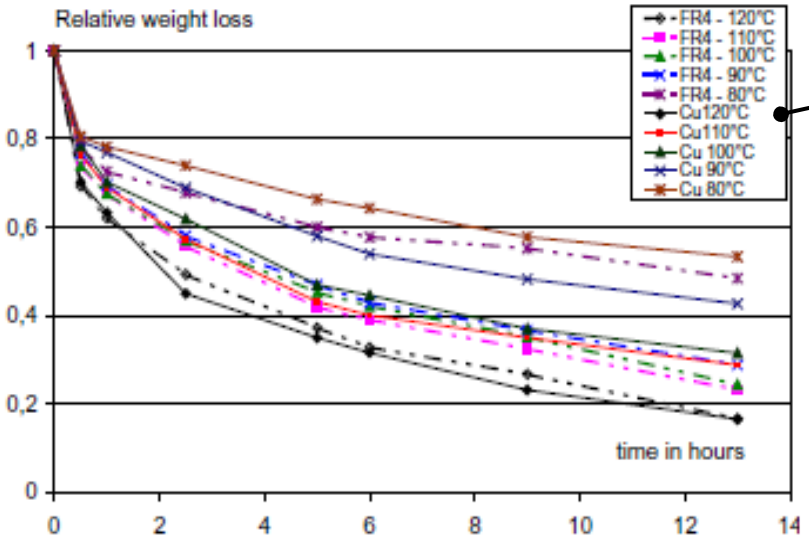
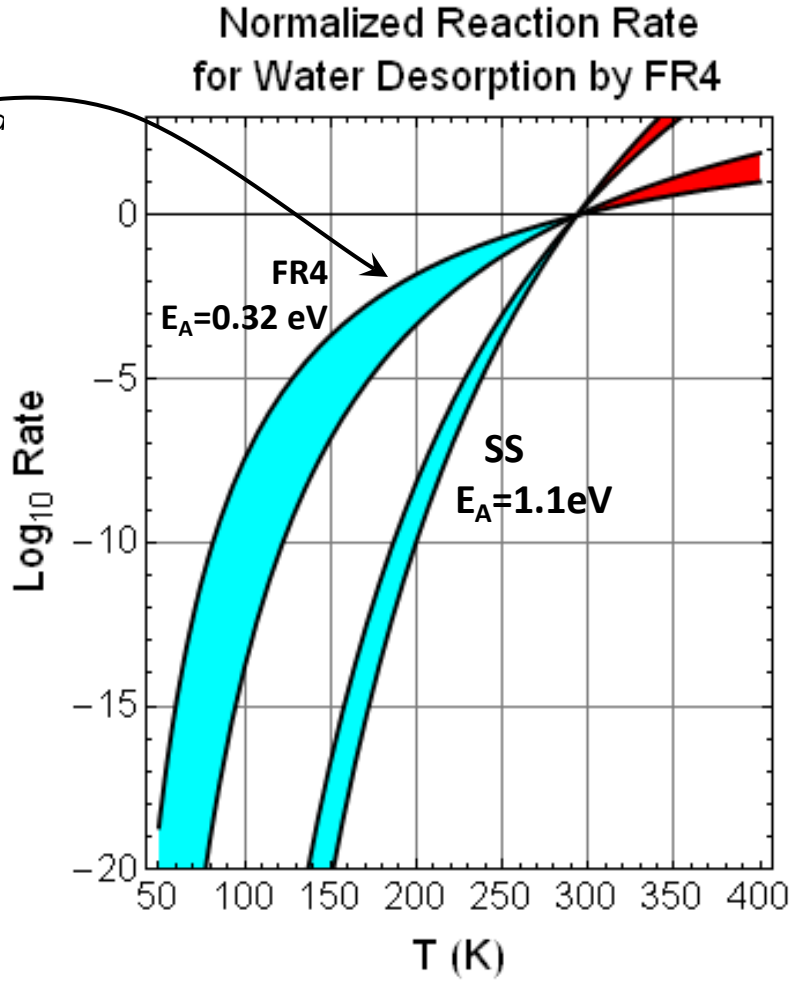


Fig. 3. Relative weight loss for 2 epoxy based PCBs at different temperatures.

$k_D(T) = \mathrm{Exp}[-E_A/k(T-T_0)]$



FR4: *K. Weide-Zaage et al., Microelectronics Reliability 45 (2005) 1662*

SS: *J.H. Hendricks, Temperature Programmed Desorption Measurementsof the Binding Energy of Water to Stainless Steel Surfaces, AVS 54th Internation Symposium (2007)*

Desorption rate depends strongly on temperature

1. Keep sources of impurities in liquid or cold gas
2. Maintain large flow in gas to dominate diffusion

The Problem of Water in LAr

So we might conclude that, to a first approximation, there is no water in the GAr; it is only in the LAr or on the surfaces in LAr, and the rate of release of water from surfaces is very small.

But the measurements in the previous two slides are for water in vacuum. It is possible that there is an interaction between water and argon that alters these observations (i.e. they are not ideal gases). It is well known that the partial pressure of water in air is NOT the vapor pressure of water.

The Problem of Water in LAr

To verify or refute this, we need to answer three questions:

1. What is Henry's coefficient for water in LAr?
2. What is the adsorption isotherm for water on SS at 90K?
3. What is the adsorption rate for water on SS?

Henry's Coefficient for H_2O in LAr

It is probably small, contrary to popular opinion. If so, gas purification may not be very effective.
Can we verify this?

Henry's Coefficient for H_2O in LAr

Here is what we know about Henry's coefficient of H_2O in LAr:

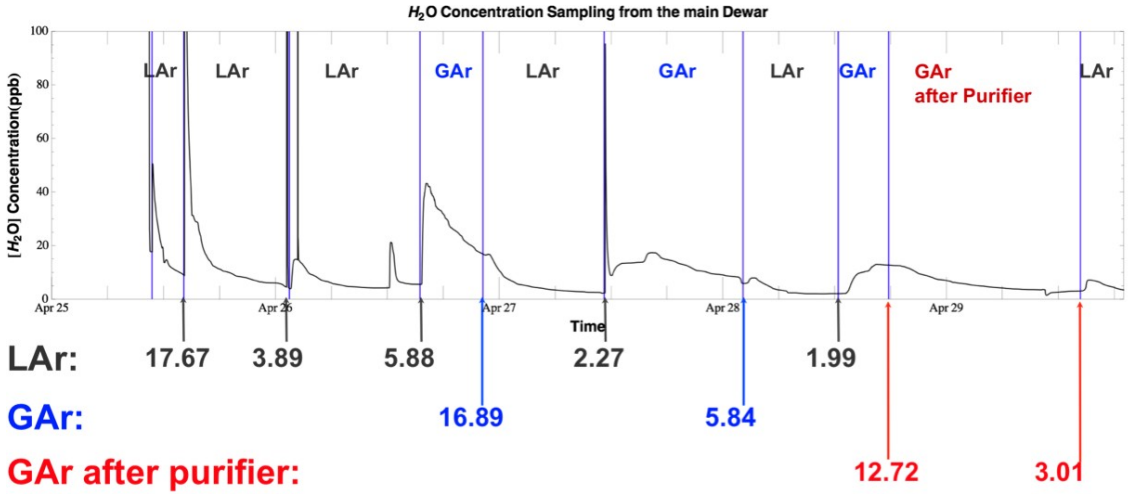
1. NIST program REFPROP v8 [1] gives $3x10^{-9}$ at 90 K , and REFPROP v10 [2] gives $4.1x10^{-3}$ at 90 K.
2. Andrews, et al. [3] report that the concentration of water in GAr is 500 times the concentration in LAr; however, this ignores the equilibrium established by Henry's coefficient and also back diffusion against evaporated gas flow, so it cannot be correct.
3. We have made measurements suggesting a value of Henry's coefficient in LAr between 0.01 and 0.4. In the two next slides we briefly explain our measurements.

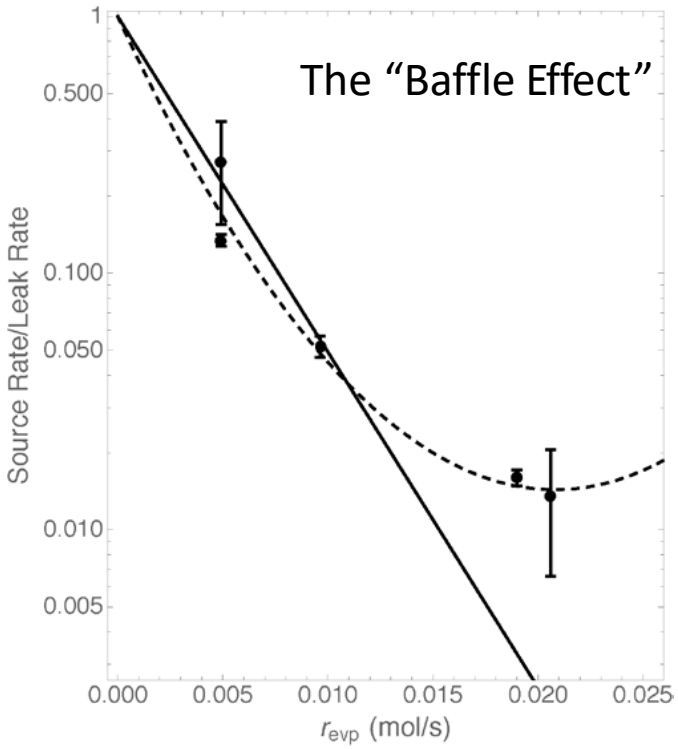
1. https://www.nist.gov/srd/refprop
2. Same source as above, but v10 uses new mixing parameters from J. Gernert and R. Span, J. Chem. Thermodyn., 93 (2016) 274: DOI:10.1016/j.jct.2015.05.015
3. R. Andrews, *et al*., NIM A608 (2009) 251.

Henry's Coefficient for Water in LAr

Method 1: By direct measurement of water in both GAr and LAr.

By alternately measuring the water concentration in the flow of gas from a tube terminating in the liquid, and from a tube terminating in the gas a few inches above the liquid, we obtain a value of H_{xx}=3.5±1.9.





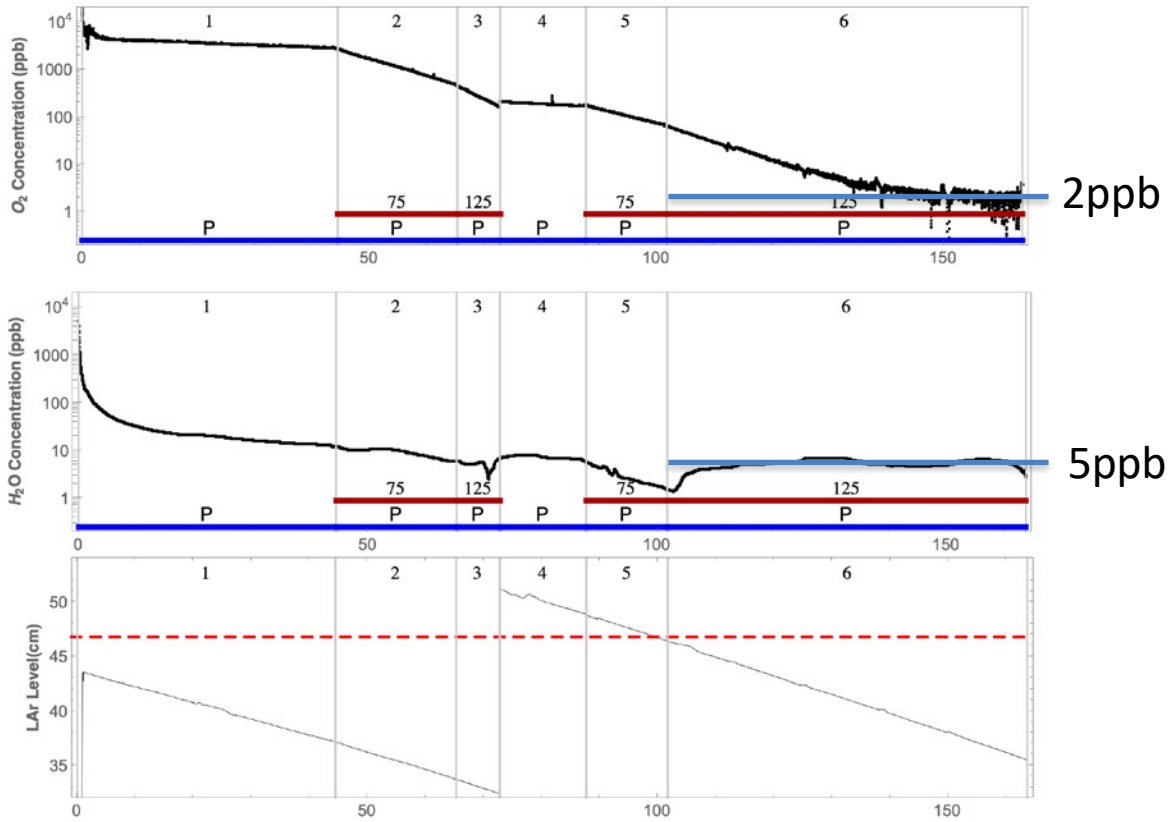
However, since the effect of diffusion against flow causes the gas above the liquid to increase with height above the surface, the true concentration in the gas at the surface is generally 10 to 100 times smaller that expected for the true leak rate. **This would imply 0.4 > H_{xx} > 0.04.**

Henry's Coefficient for Water in LAr

Method 2: Simultaneous observation of the steady state concentrations of O_2 and H_2O in LAr with purification, using Eq 2.33 of our purity paper (arXiv:2009.10906)

$$c_{i,l}^{ss} = \frac{r_{lek,i}}{H_{xx,i}\ r_{evp}\ \varepsilon_{P,i}} \quad \text{if} \quad r_{sam} \to 0$$

$$\text{assume } \varepsilon_{P,O_2} = \varepsilon_{P,H_2O} > 0$$



The ratio of H_2O to O_2 in air at 20% RH is 0.025 and at 90% is 0,1. The measured ratio of steady state concentrations is 5/2=2.5. Henry's coefficient for O_2 is 0.91.

This implies that for H_2O $0.01 < H_{xx} < 0.04$

Note also, by comparing the rate of change of concentrations for H_2O to O_2, that it is clear that adsorption dominates evaporation in determining the "cleaning" rate.

Henry's Coefficient for H_2O in LAr from the Theory of Regular Solutions

See J.H. Hildebrand and R.L. Scott, Regular Solutions, Prentice Hall, NJ (1962)

Henry's Coefficient for Impurities in LAr

from Dalton's and Raoult's Laws

Dalton's Law is

$$P_{Total} = \sum_{i=1}^{n} P_i$$

Raoult's Law is

$$P_i = x_i P_{Vap,i}$$

Therefore, for the gas phase of a two component (Z in LAr)

$$P_Z = x_Z P_{Vap,Z}$$

$$P_{Ar} = (1 - x_Z) P_{Vap,Ar}$$

x is mole fraction in liquid
y is mole fraction in gas
$x_1 = 1 - x_2$

And Henry's coefficient is

$$H_{xx} = \lim_{x \to 0} \frac{y}{x}$$

$$y = \frac{P_Z}{P_{Total}} = \frac{x_Z P_{Vap,Z}}{x_Z P_{Vap,Z} + (1 - x_Z) P_{Vap,Ar}}$$

$$H_{xx} = \lim_{x_Z \to 0} \frac{P_{Vap,Z}}{x_Z P_{Vap,Z} + (1 - x_Z) P_{Vap,Ar}} = \frac{P_{Vap,Z}}{P_{Vap,Ar}}$$

This is the result for an "**Ideal Solution**", in which both components in both phases behave as ideal gases, and there is no heat of mixing (We ignore the fact that somehow these ideal gases condense).

Henry's Coefficient for Impurities in LAr

for "Ideal Solutions"

Henry's coefficient for Ideal Solution is $H_{xx} = \frac{P_{Vap,Z}}{P_{Vap,Ar}}$

Henry's coefficients for Ideal Solutions

Species	H_{xx} Ideal	H_{xx} Meas	Ideal/Meas
Ar	1.	1	1.
N2	2.7	3.5	0.77
O2	0.74	0.9	0.83
CO	1.8	2.8	0.64
CH4	0.081	0.12	0.67
C2H6	8.2×10^{-6}	0.000077	0.11
C3H8	$3. \times 10^{-9}$	$7. \times 10^{-8}$	0.043
CF4	0.00076	0.0012	0.63

For many impurities in LAr the "Ideal Solution" model is not too bad!

Henry's Coefficient for H_2O in LAr

for an "Ideal Solution"

Henry's coefficient for H_2O in LAr is $H_{xx} = \frac{P_{Vap,H_2O}}{P_{Vap,Ar}}$

For the vapor pressure of ice, see Rainer Feistel, and Wolfgang Wagner, *Sublimation pressure and sublimation enthalpy of H_2O ice **Ih** between 0 and 273.16 K*, Geochimica et Cosmochimica Acta **71** (2007) 36.

The range of the measured data set is stated to be 273.15K $\geq$ T $\geq$ 130K, corresponding to pressures ranging from 6.11×10^{-3} bar to 4.78×10^{-13} bar. There are 216 data points in the set. Below 130K the sublimation pressure is constrained by thermodynamic relations.

From their Table 4 of this reference, the vapor pressure of ice at 90K is 1.39×10^{-22} bar. The vapor pressure of LAr at 90K is 1.33 bar.

This gives Hxx = 1.04×10^{-22} at 90K – could it really be this small?

- If not, there must be a large chemical interaction between water and LAr.
- This is actually the case for water vapor in air – absolute humidity is greater than the vapor pressure of water divided by atmospheric pressure.

Henry's Coefficient for a "***Regular Solution***": chemical interaction

A "Regular Solution" model improves the "Ideal Solution" model by allowing heat of mixing, but requires that the entropy change be that of the ideal solution, namely $-R\, x_i\, ln(x_i)$ per mole.

Then, Henry's coefficient for impurity 1 in solvent 2 is

$$H_{xx} = \frac{P_{Vap,1}}{P_{Vap,2}} Exp\left(\frac{v_{M,1}}{R\,T} \left(c_{11} + c_{22} + 2(1 - L_{12})\sqrt{c_{11} c_{22}} \right) \right)$$

where

$$c_{ii} = -\Delta H_{Vap} / v_{M,i}$$

$v_{M,i}$ = molar volume of i

c_{ii} is the "cohesive energy" of component i.

$c_{i2} = (1\text{-}L_{12})\,(c_{11}\, c_{22})^{1/2}$ defines L_{12}, a parameter that is near zero when solute and solvent are similar.

J.H. Hildebrand and R.L. Scott, Regular Solutions, Prentice Hall, NJ (1962)

J.M. Prausnitz, Molecular Thermodynamics of Fluid-Phase Equilibria, Prentice-Hall, Englewood Cliffs NJ (1969) 263 *et seq*.

E.R. Bazua and J.M. Prausnitz, *Vapor - liquid equilibria for cryogenic mixtures*, Cryogenics 11 (1971) 114.

Henry's Coefficient for "Regular Solutions"

Henry's coefficient for a "Regular Solution" is

$$H_{xx} = \frac{P_{Vap,1}}{P_{Vap,2}} Exp\left(\frac{v_{M,1}}{R\,T} \left(c_{11} + c_{22} + 2(1 - L_{12})\sqrt{c_{11}c_{22}} \right) \right)$$

Henry's coefficients for Regular Solutions

Species	H_{xx} Reg	H_{xx} Meas	L_{12}	Reg/Meas
Ar	1.	1	0	1.
N2	3.5	3.5	−0.014	0.998
O2	0.91	0.9	0.011	1.01
CO	2.6	2.8	0.005	0.92
CH4	0.12	0.12	0.018	0.991
C2H6	0.000077	0.000077	0.012	1.
C3H8	7.1×10^{-8}	$7. \times 10^{-8}$	0	1.01
CF4	0.0012	0.0012	0	0.96
H2O	1.9×10^{-8}	1.	0	1.9×10^{-8}
H2O	1.	1.	0.49	1.

} ?

Good agreement with measurements!

Henry's coefficients and Solubilities in LAr

Solute	H_{xx}	x_2 Max	Reference
N_2 (*g*)	3.5	1	1, 2, 8, 12
O_2 (*l*)	0.9	1	1, 8, 12, 24, 25, 26, 27, 28
He (*g*)	4150	?	10
Ne (*g*)	955	0.9	10, 11, 13, 14, 15
Kr (*s*)	2.2	0.35	1
Xe (*s*)	$<10^{-5}$	0.05	16
H_2 (*g*)	780	0.25	5, 9
D_2 (*g*)	610	?	5
CO (*g*)	2.8	1	1, 12
CO_2 (*s*)	?	2.6×10^{-6}	3, 4, 6
CH_4 (*s*)	0.12	?	1, 2, 7
CF_4 (*s*)	0.0012	?	1
Ethane (*s*)	0.000077	?	1
Propane (*l*)	$7.\times10^{-8}$	?	1
1,3–Butadiene (*s*)	?	$9.\times10^{-7}$	3
Pentane (*s*)	?	9.4×10^{-6}	3, 18
2–Methylbutane (*s*)	?	0.000014	17, 18
Neopentane (*s*)	?	0.00082	3
1–Pentene (*s*)	?	$7.\times10^{-7}$	17
Isoprene (*s*)	?	2.4×10^{-6}	23
Cyclopentane (*s*)	?	9.3×10^{-8}	3, 18, 22
Cyclopentene (*s*)	?	7.1×10^{-6}	21
Hexane (*s*)	?	1.4×10^{-7}	19
2–Methylpentane (*s*)	?	2.3×10^{-7}	20
1–Hexene (*s*)	?	6.7×10^{-7}	20
1–Hexyne (*s*)	?	1.5×10^{-7}	21
Cyclohexane (*s*)	?	1.6×10^{-7}	19
2,3–Dimethylbutane (*s*)	?	$7.\times10^{-7}$	3, 22
H_2O (*s*)	2	$3.\times10^{-7}$	4, 26, 28
N_2O (*s*)	?	0.000074	4
Dimethyl ether (*s*)	?	0.000013	4
Diethyl ether (*s*)	?	4.5×10^{-6}	4
Di–n–propyl ether (*s*)	?	3.7×10^{-6}	4
Di–isopropyl ether (*s*)	?	$2.\times10^{-7}$	4

We need to determine both the Henry coefficient for water in LAr and the maximum solubility of water in LAr and GAr

NIST program REFPROP gives
$H_{xx} = 3.4\text{x}10^{-9}$ for H_2O in LAr at 90K

"The solubilities of H_2O, H_2S, CH_3OH and C_2H_5OH in LN_2 (115 K), LO_2 (135 K) and LAr (128 K) were therefore found to be below the limit of detection using IR spectroscopy, i.e. considerably less than 10^{-8} mole fraction."

A.J. Rest, R.G. Scurlock and M.F. Wu, *The Solubilities of Nitrous Oxide, Carbon Dioxide, Aliphatic Ethers and Alcohols, and Water in Cryogenic Liquids*, Chemical Engineering Journal, 43 (1990).

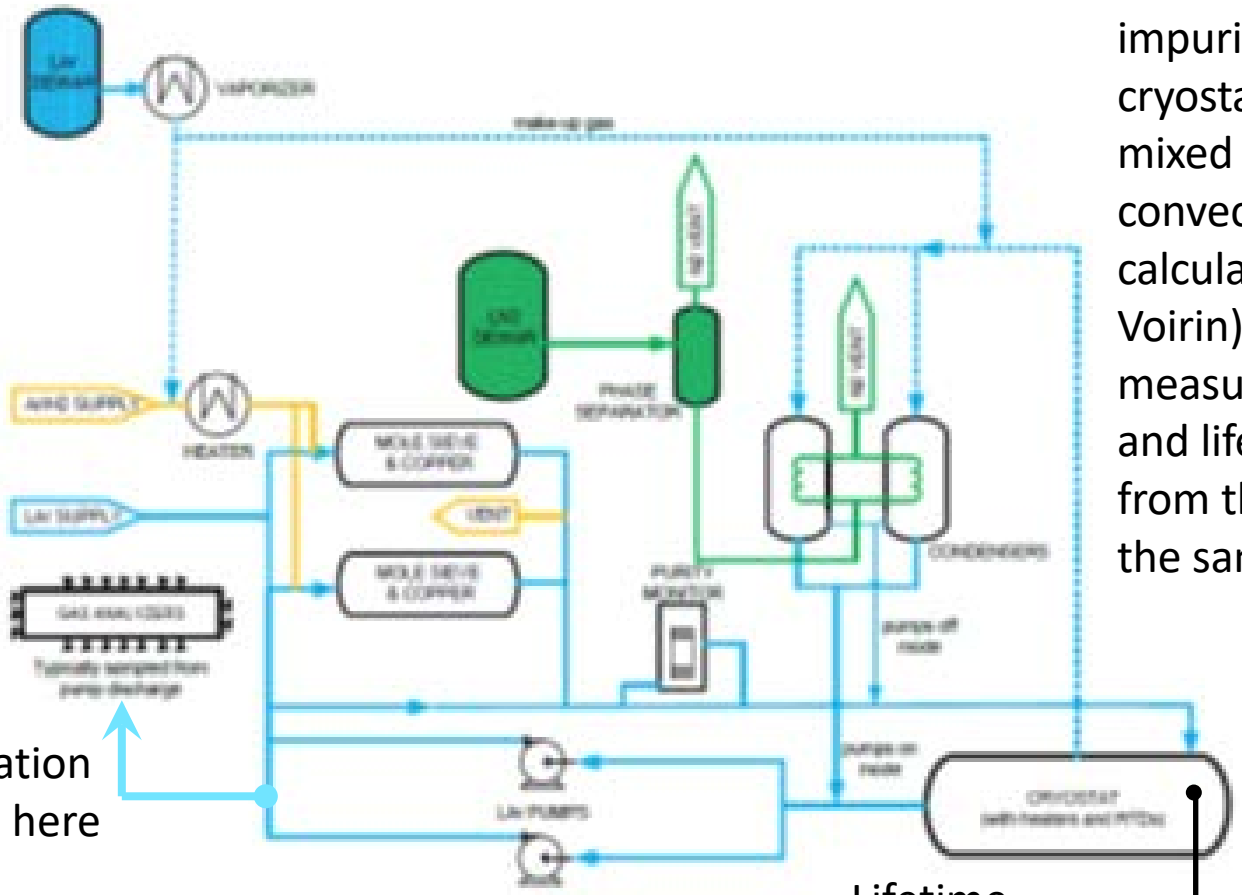
Electron Attachment to Water:

There are no experiments designed to measure attachment, but there is some "found" data

Estimate of Attachment Rate for H_2O

Carls and M. Zuckerbrot, MicroBooNE docDB 4823, 10/27/2015 made simultaneous measurements of water concentration and electron lifetime in LAr during the initial operation of MicroBooNE. This is the PID for the cryogenic system.

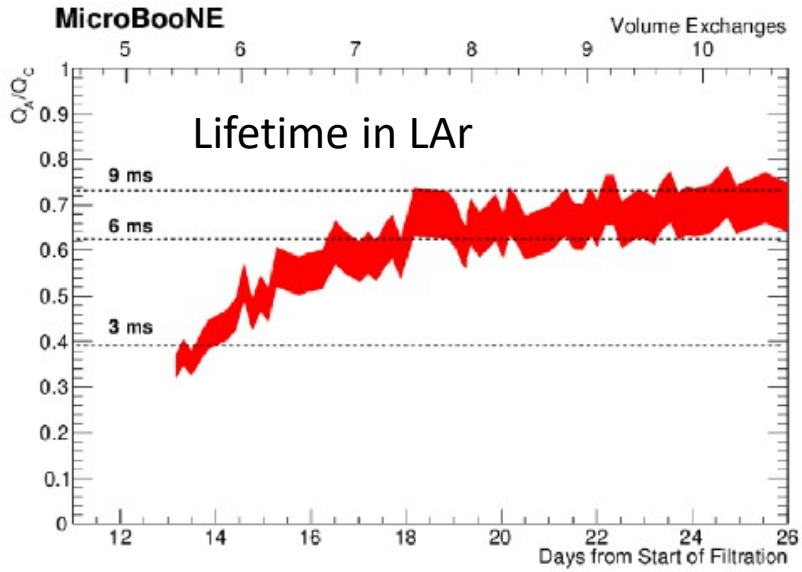
We assume that impurities in the LAr in the cryostat are thoroughly mixed by thermal convection (per CFD calculations by Erik Voirin), so we consider the measurement of purity and lifetime to be taken from the same sample at the same time.

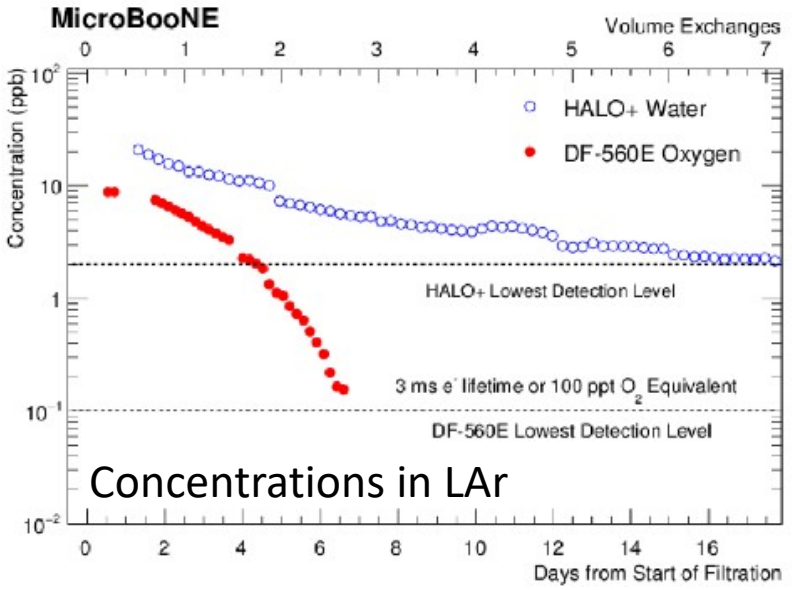


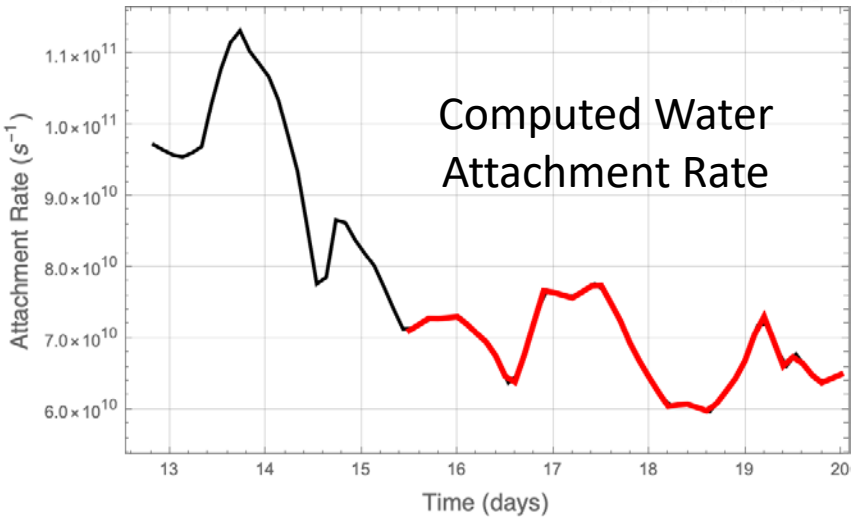
Concentration measured here

Lifetime measured here

Carls and M. Zuckerbrot: Data for Attachment Rate for H_2O







Average value for data from 15.4 to 20 hrs is $k_A(H_2O) = (6.9 \pm 0.5) \times 10^{10}\ s^{-1}$.

Average value of all data is $k_A(H_2O) = (7.8 \pm 1.5) \times 10^{10}\ s^{-1}$.

An Observation of Water Concentration in GAr and Electron Lifetime in LAr

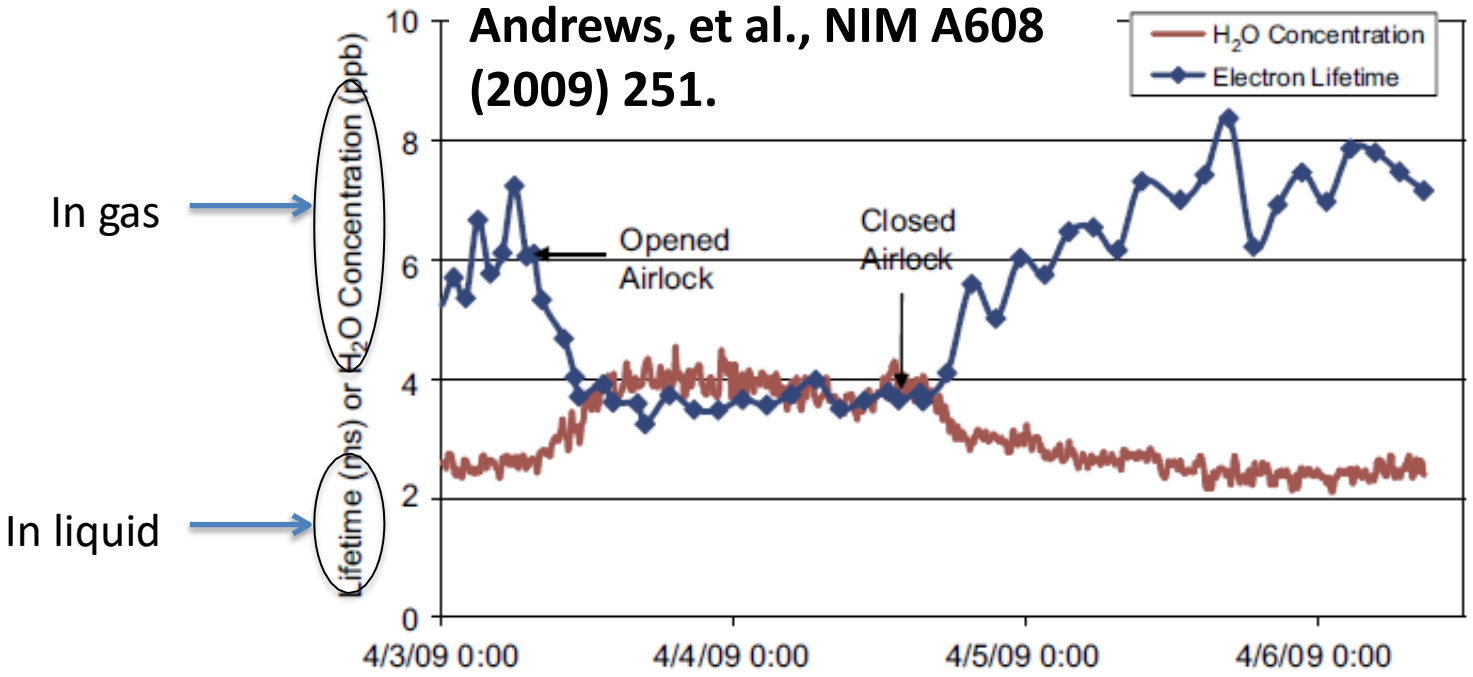


Fig. 7. Effect of connecting cryostat and airlock volumes. The cryostat was connected to the airlock by opening the gate valve that typically separates the two. Prior to opening, the airlock was under vacuum. The increase in water concentration is attributed to the additional warm metal surface area in contact with the argon vapor. The relationship between water concentration and drift lifetime is similar to the relationship observed during materials testing (e.g. Fig. 8). This test was performed with 15 in. LAr in the cryostat.

An Observation of Water Concentration in ***GAr*** and Electron Lifetime in ***LAr***

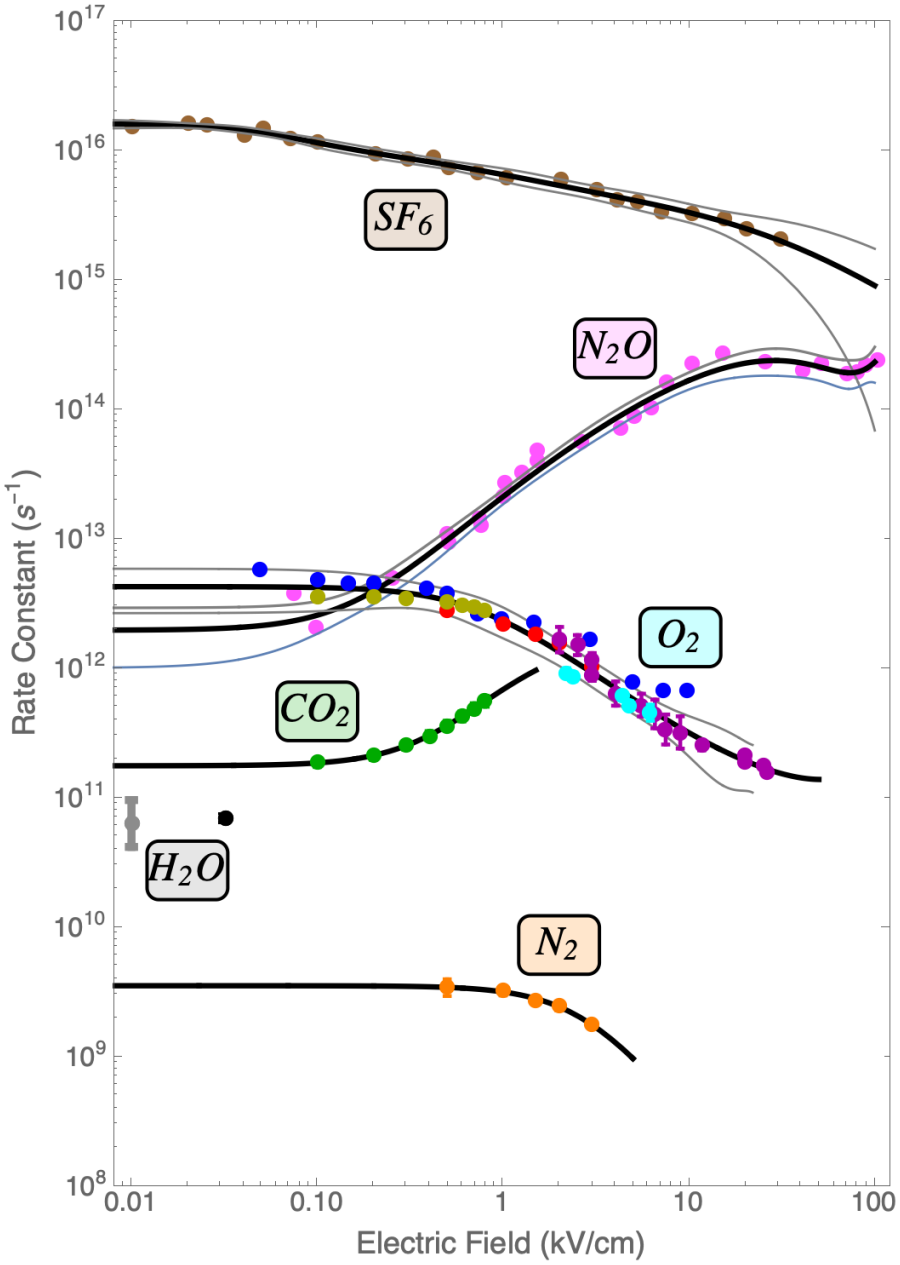
Andrews, et al., NIM A608 (2009) 251.

"When using the sintered metal return and operating the internal filter, we estimate the water concentration in the liquid is 1/500 of that in the vapor. The sintered metal leaves only 1/10 of the impurities in the condensate; this ratio is further reduced by the internal filter, which filters liquid 50 times faster than the condenser adds liquid."

This ignores the fact that the liquid and gas are in contact at the gas-liquid surface, where exchange of water occurs very rapidly. This is the dominant rate process and*, independent of the amount of water that is deposited into either LAr or GAr*, establishes a concentration ratio equal to Henry's constant, which we believe is 0.04, We also note that the gas at the measuring height in the gas volume is greater than that at the liquid surface, due to the back diffusion through the upward flowing evaporation gas by a factor of 10 to 100, so say 25.

The net effect is that the ratio of the concentration measured in the gas to that existing (unmeasured) in the liquid is 0.04 x 25 ≈ 1. Using this ratio, the data for GAr concentration and electron lifetime from Andrews, et al. , and assuming that only water contributes, gives $k_{ATT} = 6 \times 10^{10}\ s^{-1}$.

Measured Attachment Rates



1. The points are the measured values.
2. The black curves are the best fit to a Pade function constrained to $dk_A/d\mathcal{E}=0$ @ $\mathcal{E}=0$.
3. The gray curves are the 1σ error bands of the best fit.
4. For H_2O two measurements are shown: the higher field value is for the data of Carls [1] and the lower field value is for the data of Andrews [2].

1. B. Carls and M. Zuckerbrot, μBooNE DocDB 4823.
2. R. Andrews, et al., NIM A608 (2009) 251

Calculation of Electron Attachment Rates from Measured Electron Attachment Cross Sections

Rates from Cross Sections

From the definition of the attachment rate

$$\frac{dn_e}{dt} = -k_{e+X\to Y} n_e n_X$$

and the definition of the cross section

$$\frac{dn_e}{dt} = -v\sigma_{e+X\to Y}(v) n_e n_X$$

we have

$$k_{e+X\to Y} = v\sigma_{e+X\to Y}(v)$$

which, when integrated over the electron velocity distribution function, gives

$$k_{e+X\to Y} = \int_0^\infty v\rho_V(v)\sigma_{e+X\to Y}(v)\, dv$$

Converting from velocity to energy gives

$$k_{e,X} = \sqrt{\frac{2}{\mu}} \int_0^\infty \sqrt{E}\rho_E(E)\sigma_{e,X}(E)\, dE$$

see slides 30 & 31

see slides 33 & 34

Electron Energy Distribution Functions

When the electrons are in thermal equilibrium with the atoms the EEDF, $\rho E(E)$, is given by the Maxwell distribution.
In the presence of an applied external field, the electrons are heated by collisions, and the EEDF is obtained as the solution of the Maxwell-Boltzmann equation using the actual atomic scattering cross sections, $\sigma(E)$, for electron scattering in LAr.
For gasses, the solution can be obtained from the computer program MagBoltz – see http://magboltz.web.cern.ch/magboltz/
For liquids there is additional coherent scattering from atomic correlations in the liquid. Re-writing MagBoltz for liquids is not trivial.

As simple-minded substitute, we use the Maxwell distribution with a field-dependent electron energy

$$\rho_M(\mathcal{E},T) = \sqrt{\frac{4}{\pi}}\sqrt{\mathcal{E}}\left(\frac{1}{kT}\right)^{3/2} e^{-\frac{\mathcal{E}}{kT}}$$

with

$$kT = \frac{e\mathcal{D}_\perp(\mathcal{E})}{\mu}$$

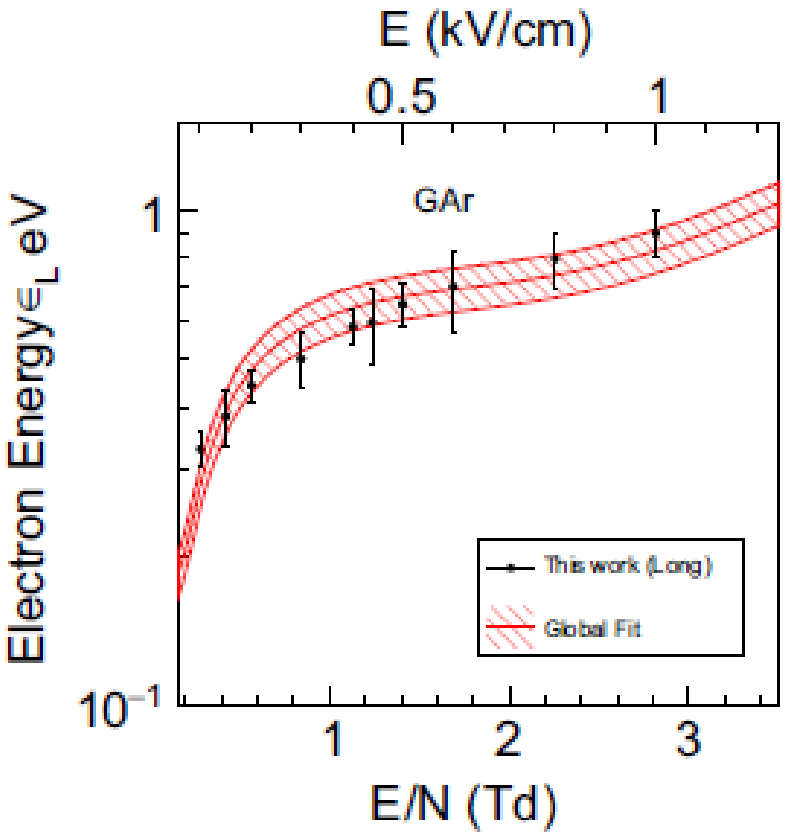
The measured transverse diffusion gives the electron temperature through the Einstein relation.

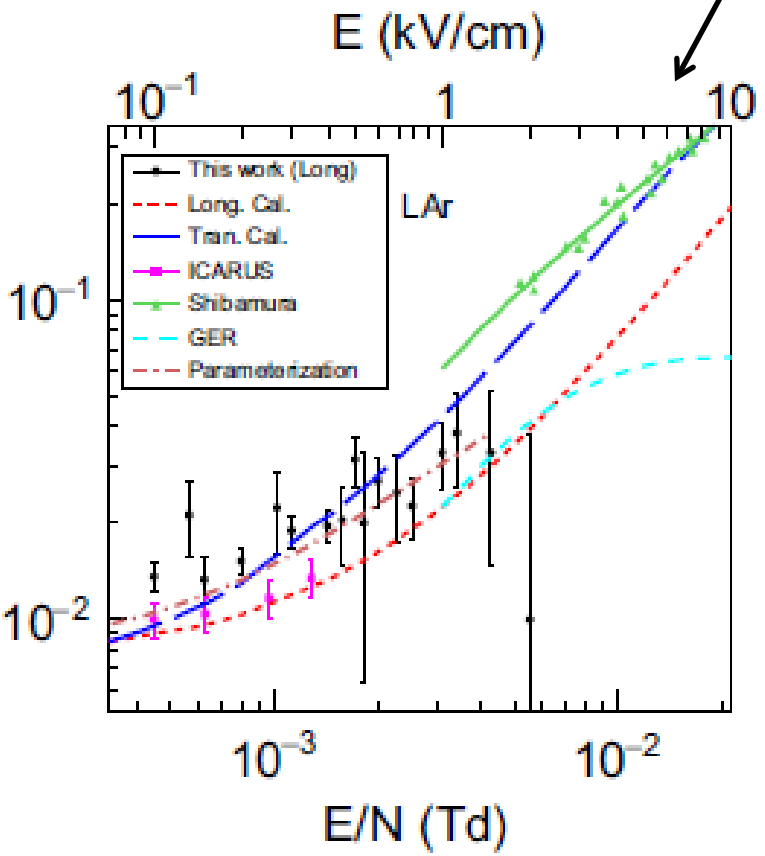
See Bakale, et al., J. Phys. Chem. 80 (1976) 2556 for a more rigorous, but still semi-empirical approach, and Atrazhev and Timoshkin, IEEE Trans. Dielectrics and Electrical Insulation 5 (1998) 450 for the solution of the Boltzman equation in liquid, including coherent scattering.

Measured Transverse Diffusion of Electrons in LAr

Measurements are consistent with Atrazhev calculation

Y. Li et al. / Nuclear Instruments and Methods in Physics Research A 816 (2016) 160–170





Attachment Mechanisms

Single step processes

1. **Direct Radiative (resonance or direct) attachment**

$$e^- + X \rightarrow X^{-*} \rightarrow X^- + \mathrm{h}\nu$$

2. **Dissociative attachment**

$$e^- + X + M \rightarrow X^- + M + k.e.$$

3. 3-body attachment

$$e^- + XY \rightarrow X^- + Y + k.e.$$

Multi-step processes (to keep things simple we do not consider these)

Multiple simultaneous and sequential single step processes

$a \rightarrow b \rightarrow c$ implies $\frac{1}{k} = \frac{1}{k_{ab}} + \frac{1}{k_{bc}}$ and $\begin{matrix} a \rightarrow b \\ a \rightarrow c \end{matrix}$ implies $k = k_{ab} + k_{ac}$

See *e.g.* Christophorou, Chem Rev 76 (1976) 409.

Equilibrium

Attachment is in equilibrium with detachment: detailed balance applies

$\begin{matrix} a \rightarrow b \\ a \leftarrow b \end{matrix}$ implies $\frac{k_{ba}}{k_{ab}} = \frac{2j_a+1}{2j_b+1} \exp(\frac{\Delta E_{ba}}{k_B T})$

Attachment Mechanisms
Summary

We consider only two processes

1. **Radiative (direct) attachment**
2. **Dissociative attachment**

1. Radiative attachment cross sections are generally not available:
   Therefore, we assume a Hauser-Feschbach type process for radiative attachment, for which $\sigma \sim \lambda^2 \sim E^{-1}$, and scale the magnitude to match the measured attachment at low electric field.

2. We take the dissociative attachment cross sections from the literature. See www.LxCat.net.

Correlation Between Electron Attachment at Zero Field and Electron Affinity

Empirical interpolation between measured values of zero-field attachment

Electron Affinities and Dissociation Energies

They are a proxy for cross section

Species	E_A (eV)	$E_{Diss, Mol}$ (eV)
SF_5	3.66	
Cl	3.61	n/a
F	3.40	n/a
SF_3	3.07	
F_2	3.01	1.60
Cl_2	2.38	2.48
SF_4	2.35	
NO_2	2.27	
O_3	2.10	
OH	1.83	4.39
O	1.46	n/a
SO	1.13	5.36
SO_2	1.11	5.67
→ SF_6	1.07	3.38
H	0.75	n/a
→ O_2	0.45	5.12
NH	0.22	3.51
→ N_2O	0.22	1.71
→ $(H_2O)_2$	0.03	3.27, 3.56, …
NO	0.026	7.59
→ H_2O	≤0	3.27, 3.56, …
NH_2	0	4.23
NH_3	0	4.66
N	-0.07	n/a
→ CO_2	-0.6	5.45
→ N_2	-1.6	9.76
CO	-1.8	11.10
H_2	-2.5	4.48

Electron affinity is the energy of this reaction:

$$e^- + X \rightarrow X^- + \Delta E_{EA}$$

Dissociation energy is the energy of this reaction:

$$XY + \Delta E_{Dissoc} \rightarrow X + Y$$

For dissociative attachment

$$e^- + XY \rightarrow X^- + Y + \Delta E_{Dissoc}$$

The threshold energy is

$$\Delta E_{Dissoc}(XY) - \Delta E_{EA}(X)$$

While every atom and molecule has an IP, they need not have an EA. There is a large class of anions which are not bound species. Many common molecules such as N_2, H_2O, and C_6H_6 do not form stable anions. In the gas phase H_2O^- decays to H_2O plus a free electron … the carbon dioxide anion is meta-stable for roughly 100 μs before it disintegrates: $CO_2^- \rightarrow CO_2 + e^-$.[2]

1.G.R. Somayajulu, *Dissociation Energies of Diatomic Molecules*, J. Chem. Phys. 33 (1960) 1541.

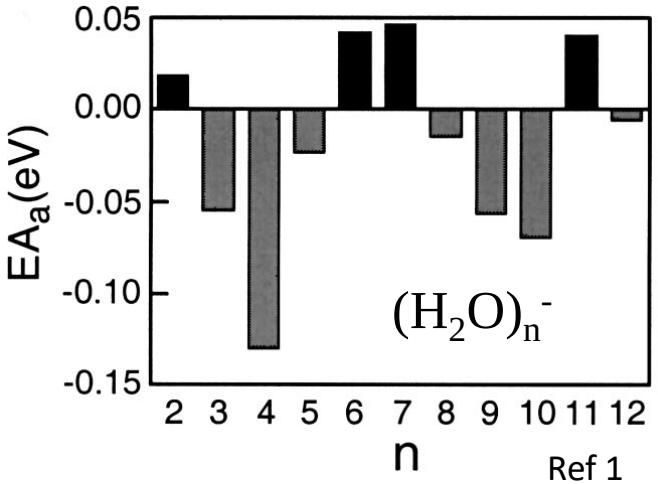
2.J.C. Rienstra-Kiracofe, et al., *Atomic and Molecular Electron Affinities: Photoelectron Experiments and Theoretical Computations*

Similar order to that for attachment rate:

$SF_6 > N_2O \sim O_2 > CO_2 > N_2$

The Electron Affinity of Water

In condensed phases of H_2O (water and ice) clusters of molecules ***do*** attach electrons to form stable anions, such as $(H_2O)_2$ with an electron affinity of 30±4 meV.



Ref 1

TABLE I. Experimental values of the adiabatic electron affinities (EA_{ad} in meV) obtained from field-detachment experiments (with the field-detachment model of Ref. 15) and of the vertical detachment energies (VDE in meV) previously obtained from photodetachment experiments.

Species	EA_{ad} (Ref. 9)	EA_{ad} (Present work)	VDE (Ref. 4)
$(H_2O)_2$	30	30±4	45±6
$(D_2O)_2$	28	26±4	42±6

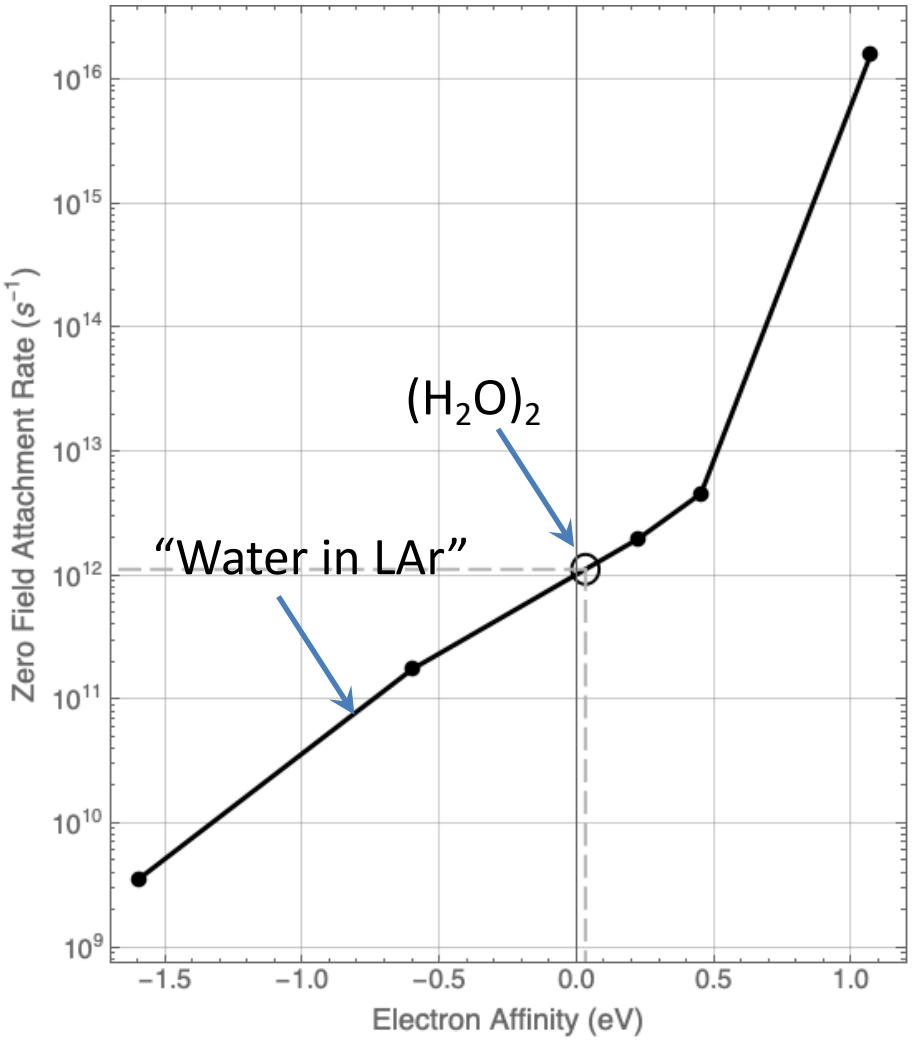
Ref 2

See:

1. H.M. Lee*, et al.*, *Origin of the magic numbers of water clusters with an excess electron*, J. Chem. Phys. **122** (2005) 044309.
2. Y. Bouteiller, *et al.*, *Structure and intermolecular motions of the water dimer anion*, J. Chem. Phys. **105** (1996) 6420.
3. A.P. Gaiduk, *et al.*, *Electron affinity of liquid water*, Nature Communications 9 (2018) 247.

Observed Correlation between Electron Affinity and Electron Attachment Rate

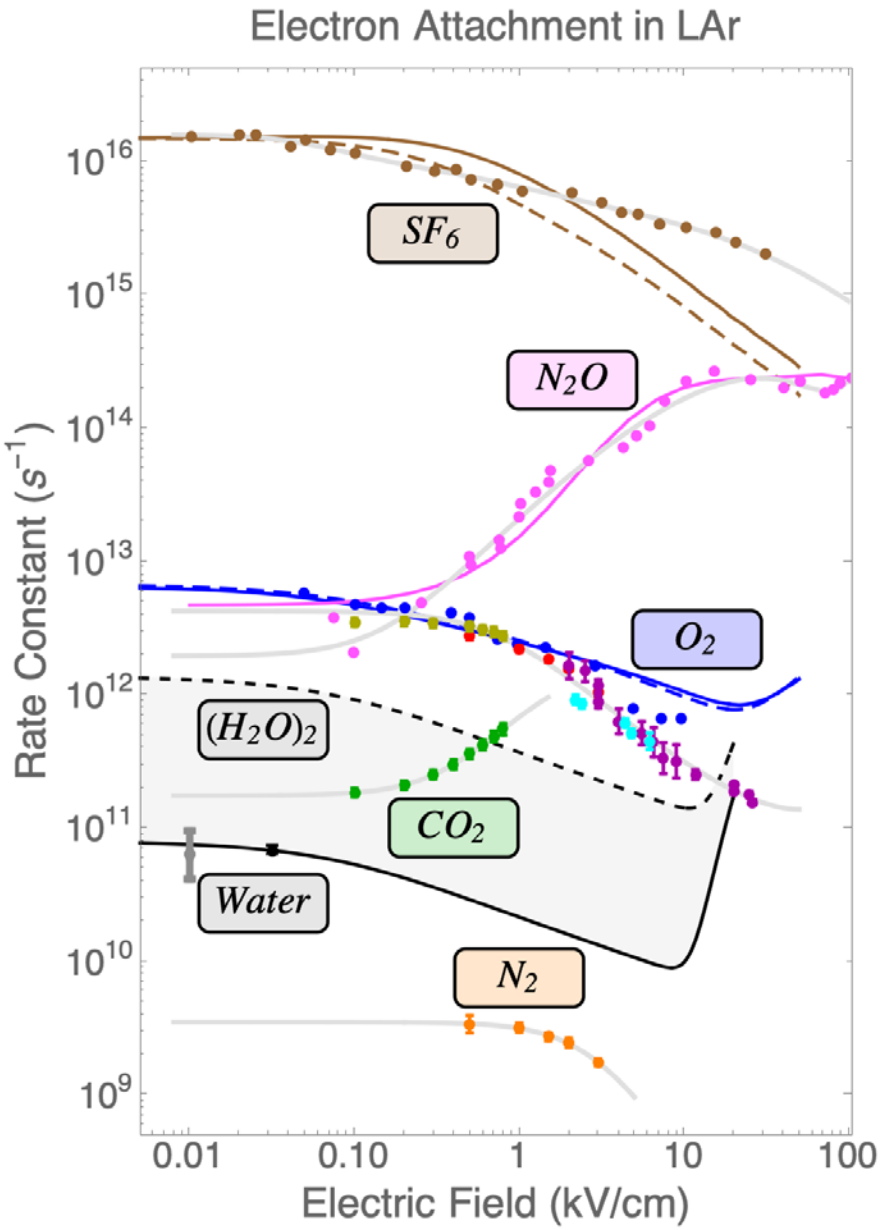
High electron affinity is associated with large direct attachment cross section.



Measured attachment rates (at zero field) and electron affinities. Negative numbers are calculations and red numbers are interpolated estimates from graph. The attachment rate for $(H_2O)_2$, is found by interpolation to be 1.13 x 10^{12} s^{-1}. By inverse interpolation the electron affinity of water in LAr is found to be -0.83 eV.

Species	$k_{ATT}[0]$ (s^{-1})	EA (eV)
SF_6	1.6 x 10^{16}	1.1
O_2	4.6 x 10^{12}	0.45
N_2O	2.0 x 10^{12}	0.22
$(H_2O_2)_2$	1.1 x 10^{12}	0.03
CO_2	1.8 x 10^{11}	-0.6
Water in LAr	6.9 x 10^{10}	-0.8
N_2	3.5 x 10^{9}	-1.6

Calculated Attachment Rates



1. The light gray curves are the best fit to a Pade function constrained to $dk_A/d\mathcal{E} = 0$ at $\mathcal{E} = 0$.
2. The solid & dashed curves in color are calculated from cross sections with the modified Maxwell energy distribution described above.
3. For H_2O two calculations are shown, each using a different magnitude of the radiative attachment cross section, but the same dissociative attachment cross section.
   a) The dashed black line matches the low field attachment implied by the measured electron affinity (see slide 31)
   b) The solid black line matches the values from our analysis of the data of Carls [1] (black point) and the data of Andrews [2] (gray point).

1. B. Carls and M. Zuckerbrot, μBooNE DocDB 4823.
2. R. Andrews, et al., NIM A608 (2009) 251

A Procedure To Define the Sources of Finite Electron Lifetimes in LAr

Measure Lifetime as a Function of O_2, N_2, and H_2O Concentrations

$$\vec{r}_A \equiv \vec{\tau}_A^{\,-1} = \vec{k}_A \bullet \vec{\vec{c}}$$

$$\vec{r}_A = \{r_{A,1}, r_{A,2}, r_{A,3}\}$$

$$\vec{k}_A = \{k_{A,O_2}, k_{A,H_2O}, k_{A,N_2}\}$$

$$\vec{\vec{c}} = \begin{Bmatrix} c_{O_2}(1) & c_{O_2}(2) & c_{O_2}(3)\ldots \\ c_{H_2O}(1) & c_{H_2O}(2) & c_{H_2O}(3)\ldots \\ c_{N_2}(1) & c_{N_2}(2) & c_{N_2}(3)\ldots \end{Bmatrix}$$

Use a minimization procedure to find the unknown k_A vector that best represents the measured rate vector, r_A, and the measured concentration matrix, c.

Can We Determine a "Residual Impurity" Concentration and Attachment Rate?

$$\vec{k}_A = \{k_{A,O_2}, k_{A,H_2O}, k_{A,N_2}, k_{A,X}\}$$

$$\overline{c} = \begin{Bmatrix} c_{O_2}(1) & c_{O_2}(2) & c_{O_2}(3) & \dots \\ c_{H_2O}(1) & c_{H_2O}(2) & c_{H_2O}(3) & \dots \\ c_{N_2}(1) & c_{N_2}(2) & c_{N_2}(3) & \dots \\ c_X & c_X & c_X & \dots \end{Bmatrix}$$

Can we also find the product $k_{A,X}\,c_X$ that best represents inner product of the measured rate vector and measured concentration matrix with a constant unknown additional impurity concentration?
Perhaps, with high precision measurements of lifetimes.

Summary

Some Estimates for Properties of Water in LAr

1. Henry's coefficient is between 0.004 and 0.04 (i.e., 0.013 within a factor of 3).
2. The attachment rate constant is 10^{12} mole/s within a factor of 10.
3. The solubility is between 10 ppb and 300 ppb.
4. The adsorbed surface coverage is of the order of several monolayers at 100 ppb.

Needed to achieve “To Do” items

1. A purity monitor that operates at fields up to at least 1 kV/cm
2. A system with low leak rate to atmosphere ($<10^{-12}$ mole/s)
3. A way to introduce controllable, small amounts of impurity into the gas and the liquid (a controlled leak valve).
4. Maintain the LAr level (compensate for the loss by sampling) to the LAr level constant.
5. Add a mass flowmeter between the purifier and the condenser to measure the evaporation rate.
6. Increase the surface area of the LAr heater to avoid boiling.
7. A mechanism to move the sampling tube across the gas-liquid interface easily and quickly, without allowing air leaks.
8. A source of Ar saturated with water to control water leak rate.
9. Use purified GAr to purge the system, including gas analyzers, before the start of measurements.
10. A baffle that can be moved from below to above the gas recirculation inlet.
11. An RGA (mass spectrometer) to measure impurities other than O_2, N_2, and H_2O

We need to understand the response of the water concentration analyzer below 1ppb.

Response of H_2O Analyzer to Gas Dilution

Moisture concentration measured in the 20L system produced by flowing GAr through either the purifier or the hot getter. The time dependence should be a simple exponential function.