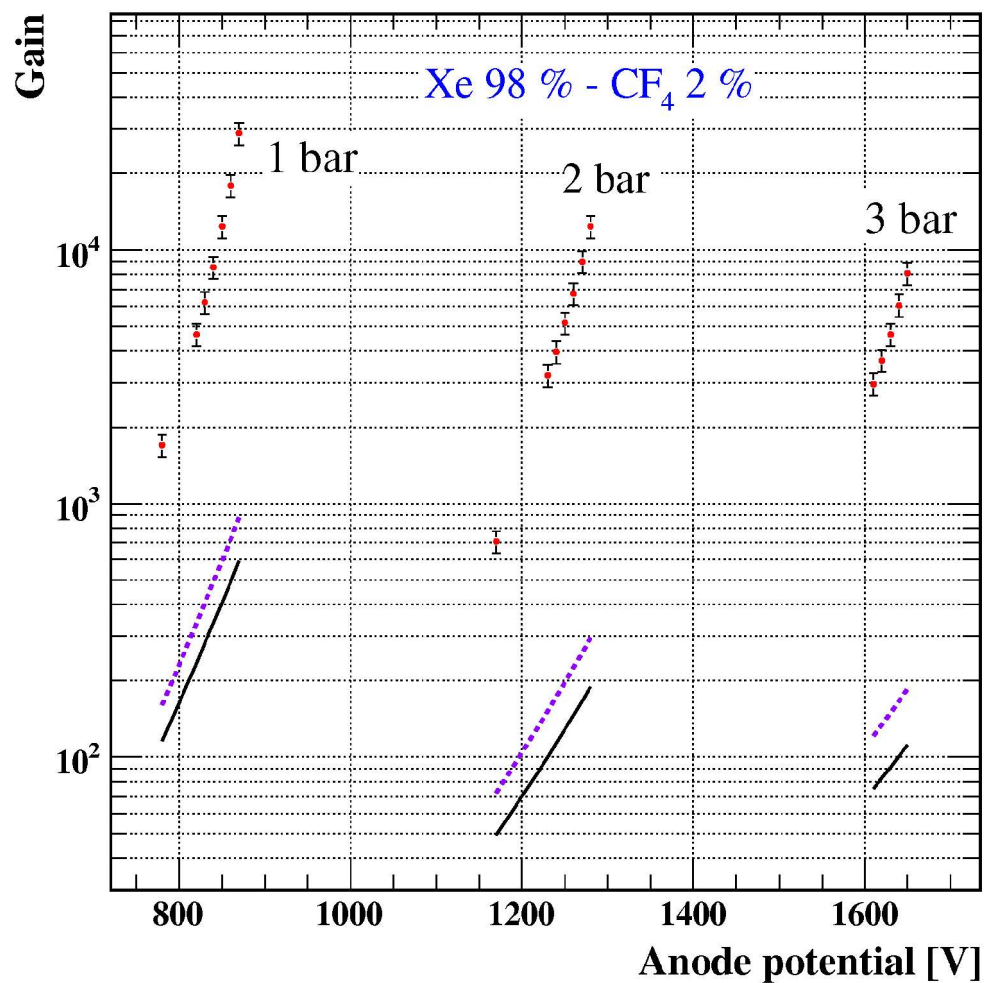
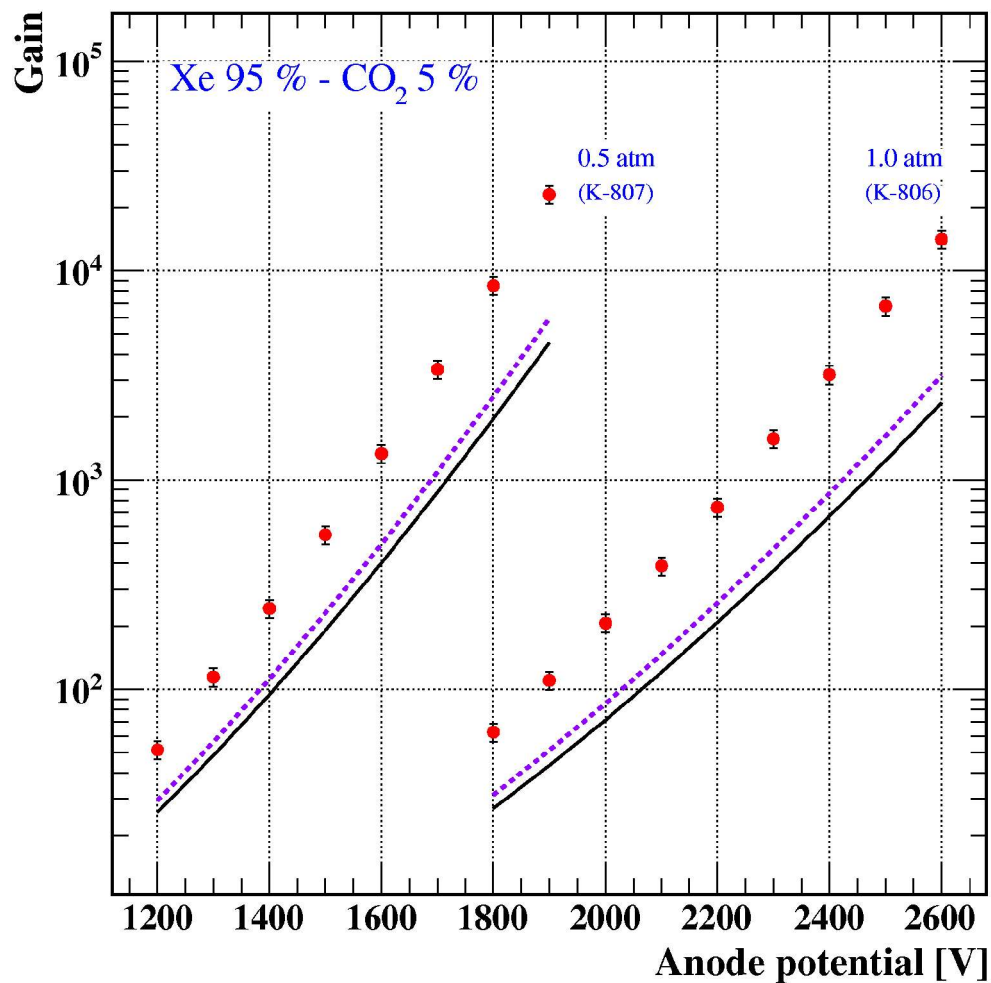


Gas gain in Xe mixtures

Ionisation cross section

Virial coefficients

Xe-CO₂ and Xe-CF₄



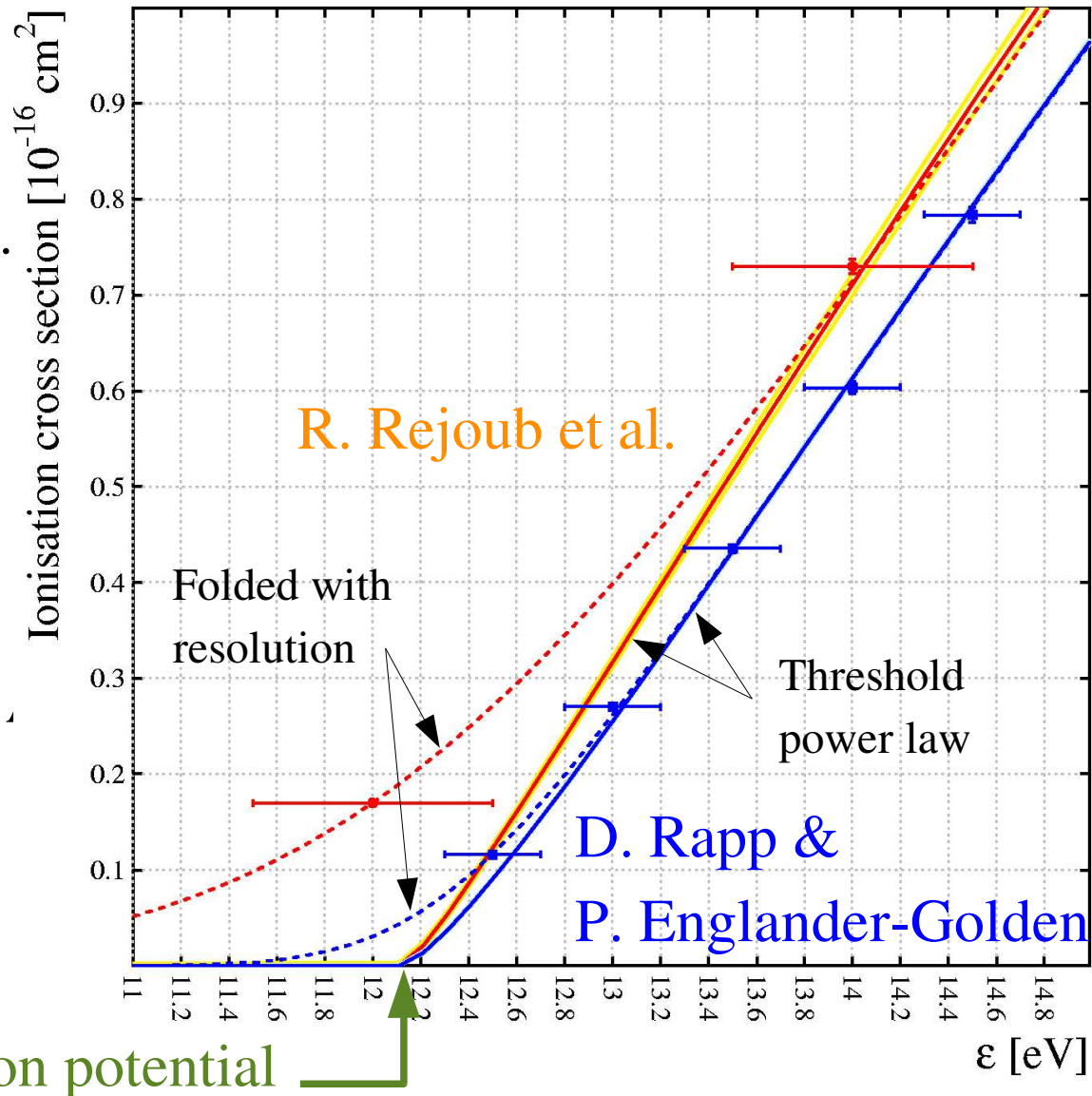
[Data: RW Hendricks, NIM A **102** (1972) 309-312, Guillaume Giroux, March 2011,
Plots: Özkan Şahin]

The problem

- ▶ The gas gain observed in Xe-CH₄, Xe-CO₂, Xe-CF₄ and other Xe-mixtures is consistently higher than calculations predict.
- ▶ Penning transfer does not occur in these mixtures because CH₄ (12.65 eV), CO₂ (13.77 eV) and CF₄ (15.90 eV) have higher ionisation potentials than Xe (12.13 eV).
- ▶ The difference is larger at higher pressure.

Ionisation cross section data

- ▶ Key measurements:
 - ▶ Donald Rapp and Paula Englander-Golden, J. Chem. Phys. **43** (1965) 1464-1479:
 - ▶ $\pm 7\%$ normalisation
 - ▶ $\pm 1\%$ relative
 - ▶ FWHM = 0.3 eV
 - ▶ R. Rejoub et al., Phys. Rev. **65** (2002) 042713 1-8:
 - ▶ $\pm 5\%$ normalisation
 - ▶ ± 0.5 eV energy scale



Ionisation cross section fit

- ▶ Although the ionisation cross section is in general difficult to calculate, simple expressions hold in the immediate vicinity of the threshold, as shown by Gregory Wannier:

$$\sigma \propto (\epsilon - \epsilon_{\text{ion}})^{\alpha}$$

- ▶ Calculation and data agree on the threshold exponent α :

$$\alpha_{\text{Wannier}} \approx 1.12689\dots = \frac{1}{2}\mu - \frac{1}{4}, \quad \mu = \frac{1}{2} \sqrt{\frac{(100Z-9)}{(4Z-1)}}, \quad Z=1$$

$$\alpha_{\text{fit}} = 1.126 \pm 0.057$$

- ▶ Impact on Townsend coefficient noticeable, but insufficient.

[Gregory H. Wannier, Phys. Rev. **90** (1953) 817-825]

Associative ionisation

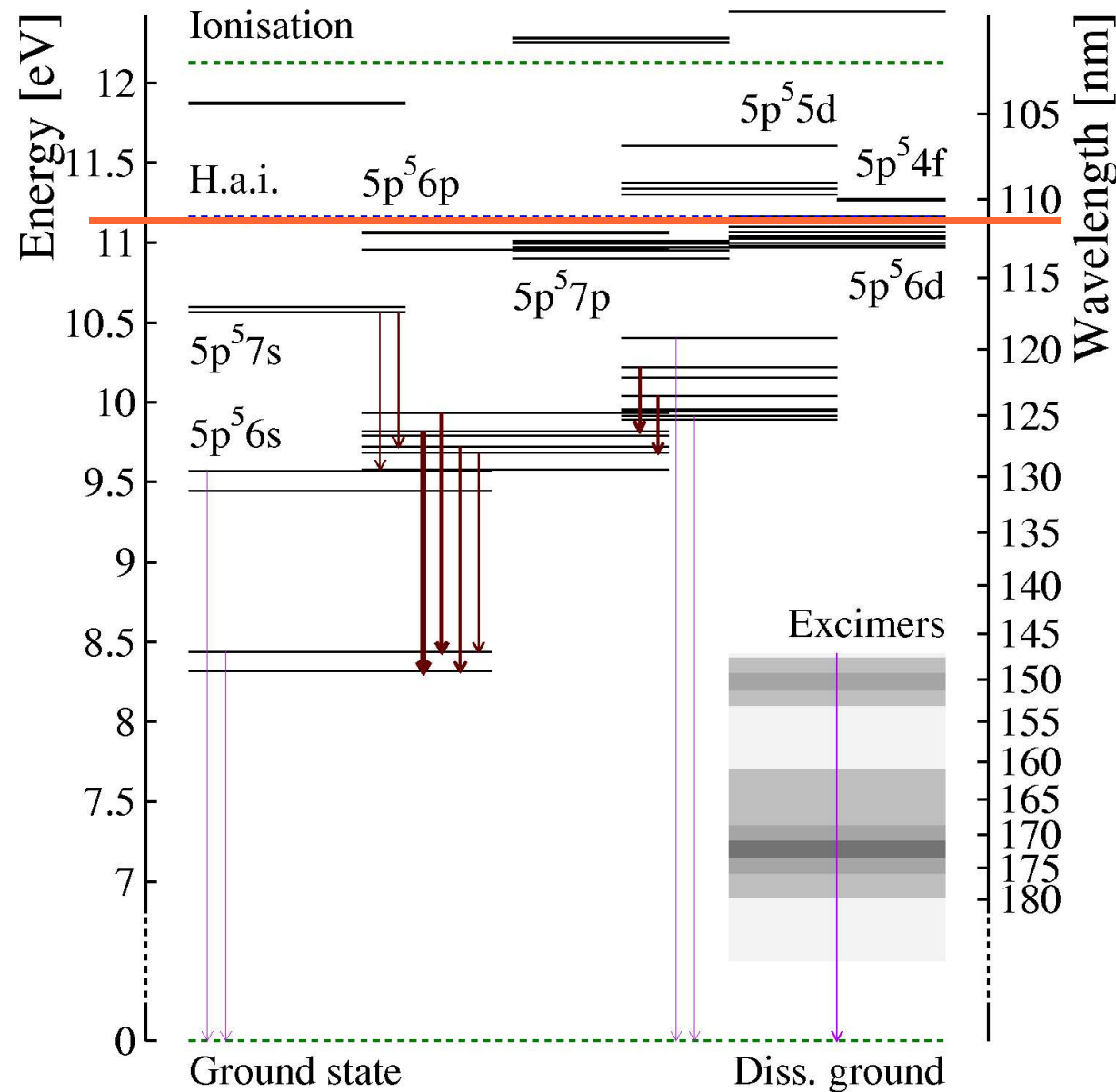
- ▶ Hornbeck-Molnar or (homonuclear) associative ionisation creates electrons from excited states:



- ▶ All $6s$, all $6p$ and the lower $7s$ doublet are below threshold (11.16 eV). The first states which can take part are $7s'$.
- ▶ Bonding is a 2-body reaction $\propto p$, hence $r_p \propto p$. This is in contrast to excimer formation which is a 3-body reaction.

Associative ionisation

► Threshold: 11.16 eV



Associative ionisation

- ▶ Associative ionisation should increase with pressure, as is indeed observed, but the fitted rates are surprisingly large:
 - ▶ CH_4
 - ▶ $p = 1 \text{ atm}$ $r_p = 50\text{-}80 \%$,
 - ▶ $p = 17 \text{ atm}$ $r_p = 200\text{-}250 \%$,
 - ▶ CO_2
 - ▶ $p = 0.5 \text{ atm}$ $r_p = 52 \%$,
 - ▶ $p = 1 \text{ atm}$ $r_p = 65\text{-}70 \%$.
- ▶ See Terry's presentation & contributions from higher levels ?

Density effects

- ▶ Like all transport properties, ionisation and excitation are affected by the density of the gas mixture.
- ▶ Magboltz automatically corrects for density effects, calculating the density N from the pressure p and the temperature T according to the ideal gas law.
- ▶ But ... Xe is not an ideal gas.

Virial expansion

- ▶ In an ideal gas:

$$1 = \frac{pV_m}{RT}$$

- ▶ In a real gas, pV_m / RT is expanded in molar volume as:

$$Z = \frac{pV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots$$

- ▶ where:

- ▶ **Z: density correction factor**, compressibility of the mixture;
- ▶ **B**: 2nd virial coefficient of the mixture;
- ▶ **C**: 3rd virial coefficient of the mixture.

Interaction virial coefficients

▶ The 2nd and 3rd virial coefficients have been compiled for numerous pure gases as function of temperature.

▶ In a mixture of 2 gases with molar fractions x_1 and x_2 :

$$B = x_1^2 B_{11} + 2 x_1 x_2 B_{12} + x_2^2 B_{22}$$

$$C = x_1^3 C_{111} + 3 x_1^2 x_2 C_{112} + 3 x_1 x_2^2 C_{122} + x_2^3 C_{222}$$

▶ B_{12} is known for most mixtures that concern us, but not C_{112} and C_{122} . Where needed, we neglect the excess coefficients:

$$B_{12} = \frac{1}{2} (B_{11} + B_{22}), \quad C_{112} = \frac{1}{3} (C_{111} + 2 C_{222}), \quad C_{122} = \frac{1}{3} (2 C_{111} + C_{222})$$

Virial coefficient tables

► We use values from the Landolt-Börnstein tables:

Landolt-Börnstein

Numerical Data and Functional Relationships in Science and Technology
New Series / Editor in Chief: W. Martienssen

Group IV: Physical Chemistry
Volume 21

Virial Coefficients of Pure Gases and Mixtures

Subvolume A
Virial Coefficients of Pure Gases

J. H. Dymond, K. N. Marsh, R. C. Wilhoit, K. C. Wong

Edited by M. Frenkel and K.N. Marsh

Landolt-Börnstein

Numerical Data and Functional Relationships in Science and Technology
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Group IV: Physical Chemistry
Volume 21

Virial Coefficients of Pure Gases and Mixtures

Subvolume B
Virial Coefficients of Mixtures

J.H. Dymond, K.N. Marsh, R.C. Wilhoit

Edited by M. Frenkel and K.N. Marsh

Examples

Xenon (cont.)

Table 2. (cont.)

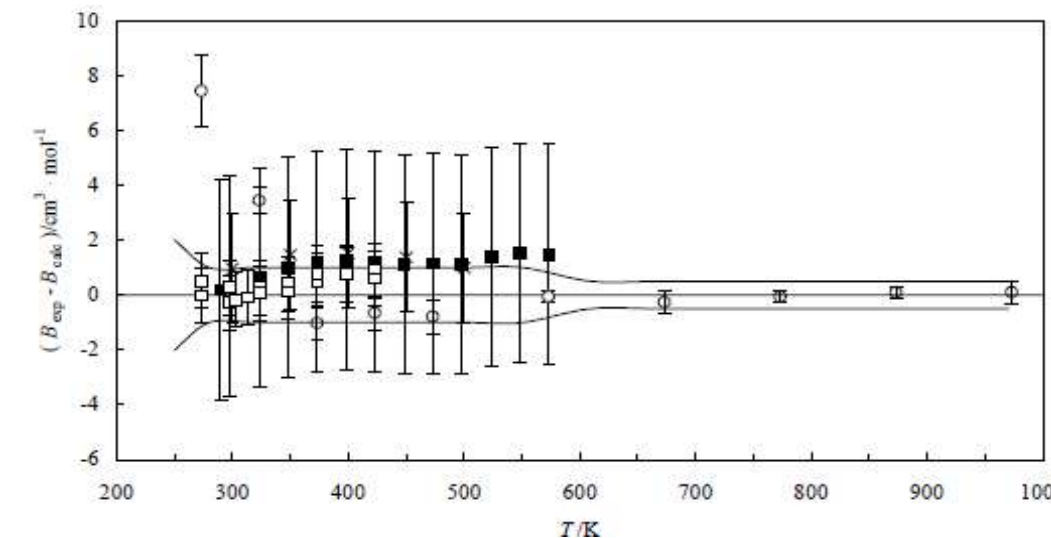
T K	$B_{exp} \pm \delta B$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$B_{exp} - B_{calc}$ $\text{cm}^3 \cdot \text{mol}^{-1}$	Ref. (Symbol in Fig. 1)	T K	$B_{exp} \pm \delta B$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$B_{exp} - B_{calc}$ $\text{cm}^3 \cdot \text{mol}^{-1}$	Ref. (Symbol in Fig. 1)
273.15	-154.7 ± 1.0	0.0	54-mic/was(□)	296.15	-136.9 ± 3.0	-4.6	82-sch/mue(□)
273.15	-154.2 ± 1.0	0.5	54-mic/was(□)	298.15	-130.2 ± 4.0	0.3	51-bea/bar-1(■)
273.15	-157.1 ± 15.0	-2.4	55-ree/why(□)	298.15	-130.3 ± 1.0	0.3	54-mic/was(□)
273.15	-147.3 ± 1.3	7.4	55-wha/lup(○)	298.15	-130.8 ± 1.0	-0.3	54-mic/was(□)
273.20	-155.0 ± 2.0	-0.3	74-hah/sch(□)	298.15	-133.0 ± 0.6	-2.5	66-gre/con(□)
276.00	-151.4 ± 2.0	0.3	80-schgeh(□)	300.00	-128.0 ± 2.0	1.0	80-per/sch(×)
276.00	-157.0 ± 3.0	-5.3	82-sch/mue(□)	300.63	-134.8 ± 2.0	-6.4	71-pol(□)
278.20	-146.9 ± 4.0	2.5	77-sch/sch(□)	303.15	-126.5 ± 1.0	-0.2	54-mic/was(□)
280.24	-153.4 ± 2.0	-6.1	71-pol(□)	303.15	-129.7 ± 15.0	-3.4	55-ree/why(□)
281.01	-151.2 ± 2.0	-4.7	71-pol(□)	309.00	-120.7 ± 4.0	1.0	77-ren/sch(□)
283.15	-147.5 ± 15.0	-3.2	55-ree/why(□)	313.15	-118.6 ± 1.0	-0.1	54-mic/was(□)
289.80	-137.8 ± 4.0	0.2	51-bea/bar-1(■)	313.15	-120.2 ± 15.0	-1.7	55-ree/why(□)
290.53	-143.3 ± 2.0	-6.0	71-pol(□)	323.15	-110.6 ± 4.0	0.6	51-bea/bar-1(■)
293.15	-139.2 ± 15.0	-4.3	55-ree/why(□)	323.15	-111.0 ± 1.0	0.3	54-mic/was(□)
293.43	-139.6 ± 2.0	-4.9	71-pol(□)	323.15	-111.2 ± 1.0	0.1	54-mic/was(□)
294.71	-136.8 ± 2.0	-3.3	71-pol(□)	323.15	-107.8 ± 0.5	3.4	55-wha/lup(○)
295.00	-132.5 ± 2.0	0.8	80-schgeh(□)	330.00	-105.4 ± 2.0	1.2	80-schgeh(□)
295.00	-138.0 ± 3.0	-4.7	82-sch/mue(□)	330.00	-111.0 ± 3.0	-4.4	82-sch/mue(□)
295.20	-131.0 ± 4.0	2.1	77-sch/sch(□)	332.00	-104.4 ± 4.0	0.9	77-ren/sch(□)

cont.

Table 1. Experimental values with uncertainty.

T K	$C_{exp} \pm \delta C$ $10^3 \text{ cm}^6 \cdot \text{mol}^{-2}$	Ref.	T K	$C_{exp} \pm \delta C$ $10^3 \text{ cm}^6 \cdot \text{mol}^{-2}$	Ref.
230.00	3.916 ± 0.500	87-hol/ha1	305.23	4.902 ± 0.400	35-mic/mic
240.00	4.968 ± 0.500	87-hol/ha1	309.65	4.100 ± 0.300	64-but/dad
250.00	5.681 ± 0.600	87-hol/ha1	313.25	4.987 ± 0.400	35-mic/mic
260.00	5.819 ± 0.600	87-hol/ha1	320.00	4.423 ± 0.400	87-hol/ha1
262.65	4.300 ± 0.300	64-but/dad	320.00	4.360 ± 0.130	90-dus/kle
270.00	5.883 ± 0.600	87-hol/ha1	320.00	4.381 ± 0.035	92-web
273.15	5.608 ± 0.400	35-mic/mic	322.86	4.928 ± 0.400	35-mic/mic
273.15	12.040 ± 2.400	50-mac/sch	323.15	4.390 ± 0.087	50-mac/sch
273.15	4.300 ± 0.300	64-but/dad	323.15	4.000 ± 0.300	64-but/dad
280.00	5.363 ± 0.600	87-hol/ha1	323.15	4.208 ± 0.400	87-hol/ha1
280.00	5.165 ± 0.155	90-dus/kle	323.15	4.128 ± 0.100	88-pat/jof
283.15	4.400 ± 0.300	64-but/dad	323.15	4.290 ± 0.186	90-glo
290.00	5.236 ± 0.500	87-hol/ha1	333.15	3.950 ± 0.300	64-but/dad
298.15	4.500 ± 1.400	80-kat/ohg	340.00	3.996 ± 0.120	90-dus/kle
298.15	6.000 ± 1.400	80-kat/ohg	343.15	3.600 ± 0.300	64-but/dad
298.15	4.905 ± 0.500	87-hol/ha1	348.15	3.670 ± 0.350	87-hol/ha1
298.15	5.664 ± 0.100	88-pat/jof	348.15	3.948 ± 0.100	88-pat/jof
298.20	4.931 ± 0.400	35-mic/mic	348.15	3.740 ± 0.175	90-glo
299.65	4.350 ± 0.300	64-but/dad	348.41	4.429 ± 0.400	35-mic/mic
300.00	4.914 ± 0.070	80-hol/wat	353.15	3.450 ± 0.300	64-but/dad
300.00	4.968 ± 0.070	80-hol/wat	363.15	2.950 ± 0.300	64-but/dad
300.00	4.946 ± 0.070	80-hol/wat	372.92	4.154 ± 0.400	35-mic/mic
300.00	4.963 ± 0.070	80-hol/wat	373.15	3.165 ± 0.063	50-mac/sch
300.00	4.927 ± 0.500	87-hol/ha1	373.15	2.650 ± 0.300	64-but/dad
300.00	4.753 ± 0.140	90-dus/kle	373.15	5.850 ± 0.290	67-ku/dod
303.05	5.160 ± 0.400	35-mic/mic	373.15	3.254 ± 0.300	87-hol/ha1
303.15	4.250 ± 0.043	55-pfe/gof	373.15	2.720 ± 0.080	88-pat/jof
303.15	4.350 ± 0.043	55-pfe/gof	373.15	3.320 ± 0.166	90-glo
304.19	5.112 ± 0.400	35-mic/mic	398.15	3.200 ± 0.320	82-ohg/nak-1
304.19	4.800 ± 0.196	90-glo	398.15	3.400 ± 0.320	82-ohg/nak-1

cont.



Carbon dioxide

[124-38-9]

CO₂

MW = 44.01

146

Xenon

[7440-63-3]

Xe

MW = 131.29

Table 2. Experimental B_{12} values with uncertainty.

T K	$B_{12} \pm \delta B_{12}$ $\text{cm}^3 \cdot \text{mol}^{-1}$	Ref.	T K	$B_{12} \pm \delta B_{12}$ $\text{cm}^3 \cdot \text{mol}^{-1}$	Ref.
223.20	-185.1 ± 2.0	67-bre	300.00	-102.2 ± 10.0	92-bel/big
273.20	-124.7 ± 2.0	67-bre	310.00	-93.6 ± 9.0	92-bel/big
290.00	-113.5 ± 10.0	92-bel/big			

Table 4. Experimental B^E values with uncertainty.

T K	x_1	$B^E \pm \delta B^E$ $\text{cm}^3 \cdot \text{mol}^{-1}$	Ref.	T K	x_1	$B^E \pm \delta B^E$ $\text{cm}^3 \cdot \text{mol}^{-1}$	Ref.
223.30	0.500	44.8 ± 0.2	67-bre	300.00	0.500	25.0 ± 1.0	92-bel/big
273.20	0.500	27.4 ± 0.2	67-bre	310.00	0.500	25.0 ± 1.0	92-bel/big
290.00	0.500	24.0 ± 1.0	92-bel/big				

Calculating the compressibility

- ▶ p and T should be known and R is a constant.
- ▶ B and C for a given T are interpolated from tables.
- ▶ V_m can formally be solved from:

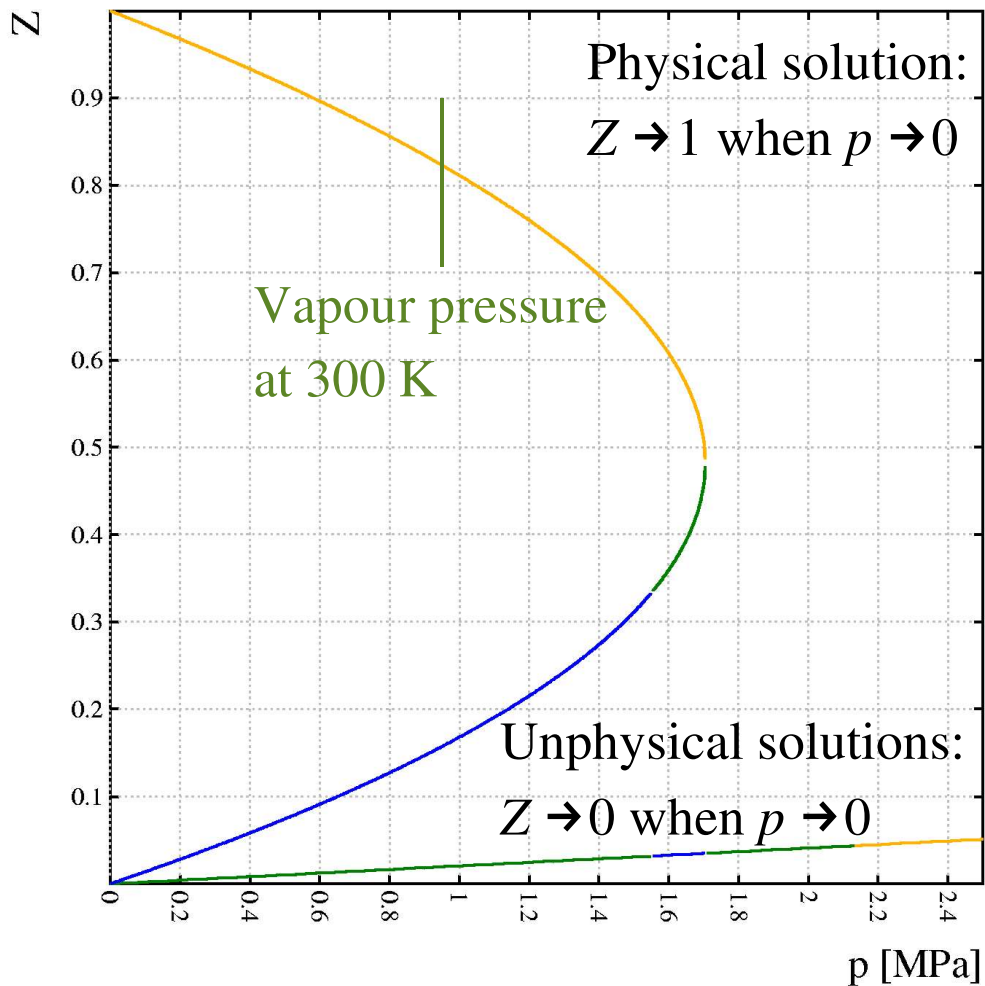
$$\frac{pV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots$$

- ▶ This yields up to 3 roots for V_m none of which is necessarily physical, some may be complex.
- ▶ The selected V_m solution, if any, is substituted in

$$Z = 1 + \frac{B}{V_m} + \frac{C}{V_m^2}$$

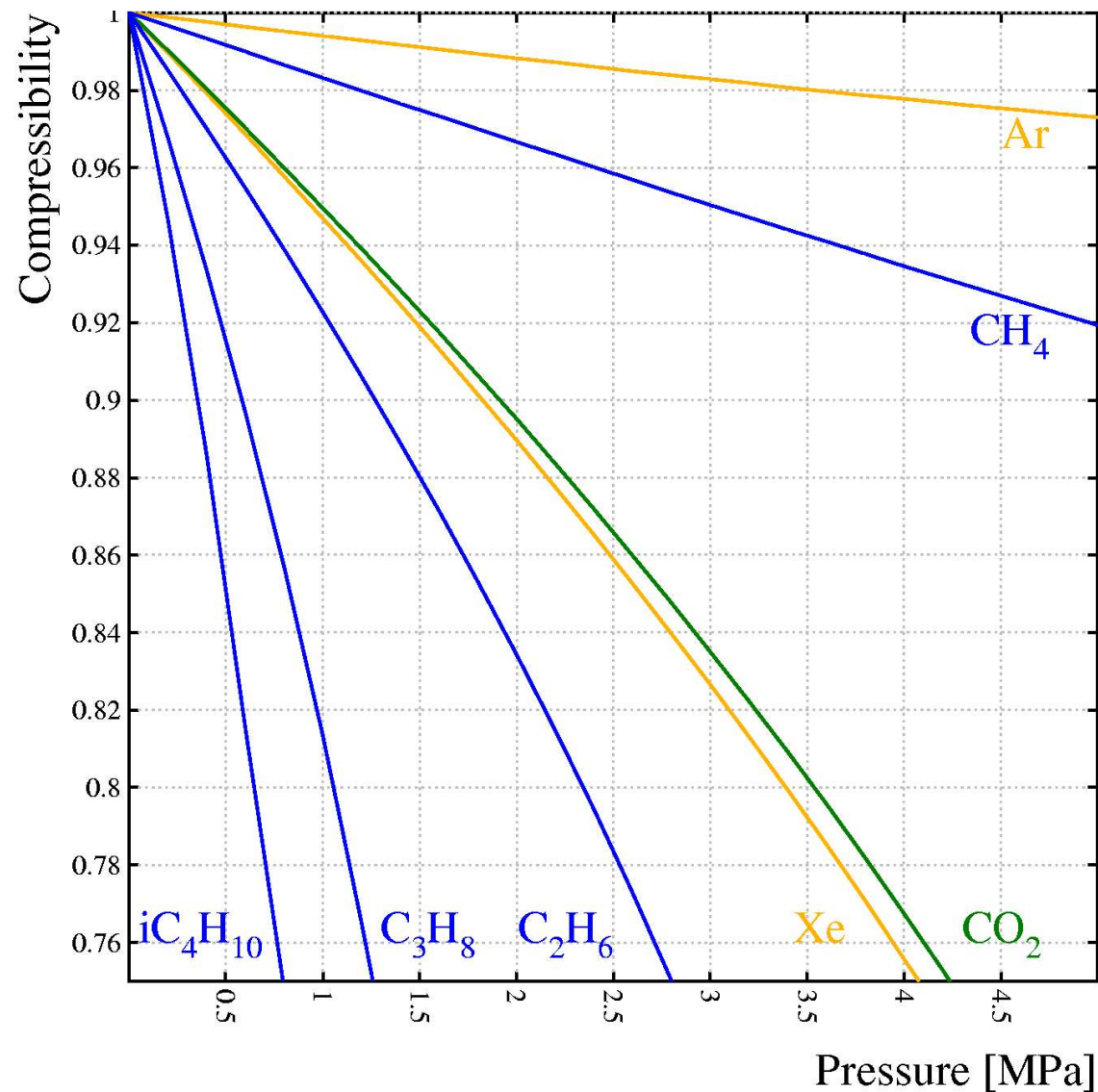
Example of compressibility

► Pure C_3H_8 at $T = 300$ K:



Compressibilities for common gases

- ▶ $Z < 1$ for all our gases !
- ▶ Corrections at $p < 5$ bar are $< 0.5\%$ in argon and $< 3\%$ in xenon.



Implications of $Z < 1$

- ▶ When $Z < 1$, the true molar volume is smaller by a factor Z than the ideal gas law predicts:

$$\frac{p V_m^{\text{true}}}{RT} = Z < 1, \quad \frac{p V_m^{\text{ideal}}}{RT} = 1, \quad \frac{V_m^{\text{true}}}{Z} = V_m^{\text{ideal}}$$

- ▶ Equivalently, the number density is N larger by a factor Z :

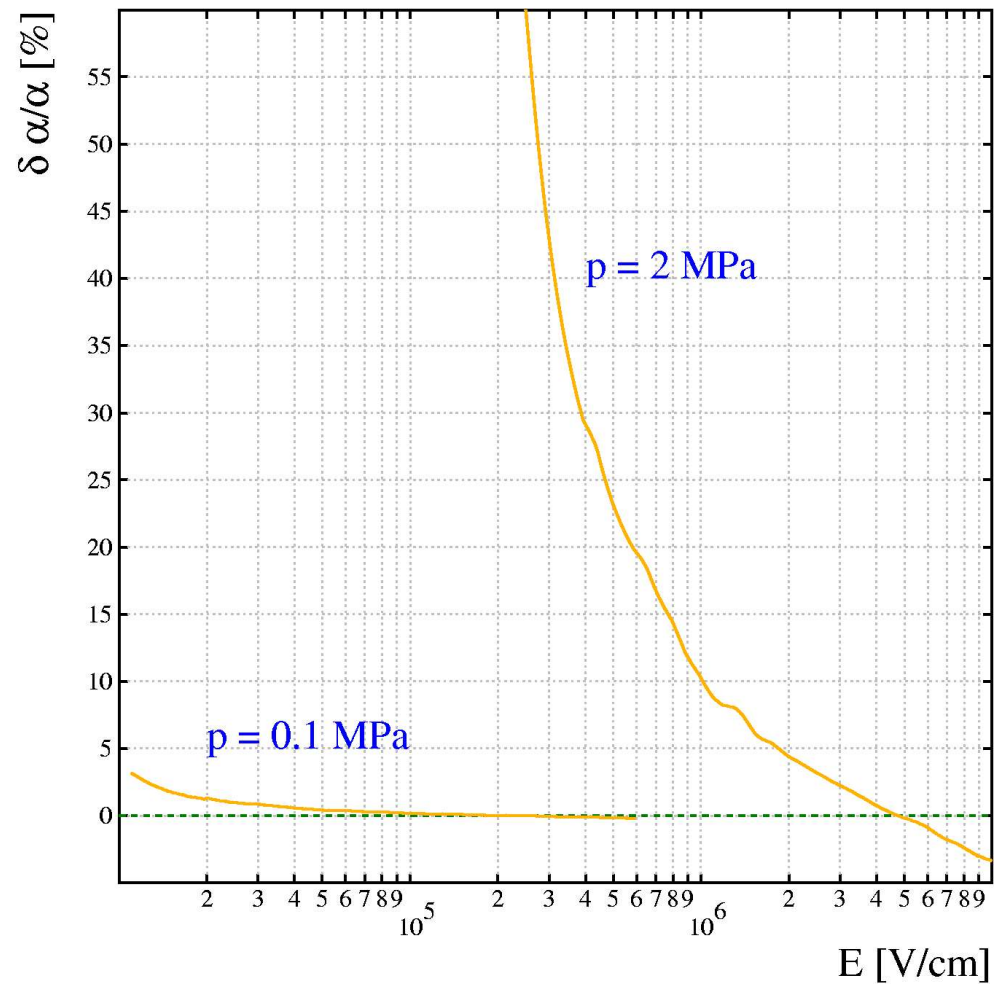
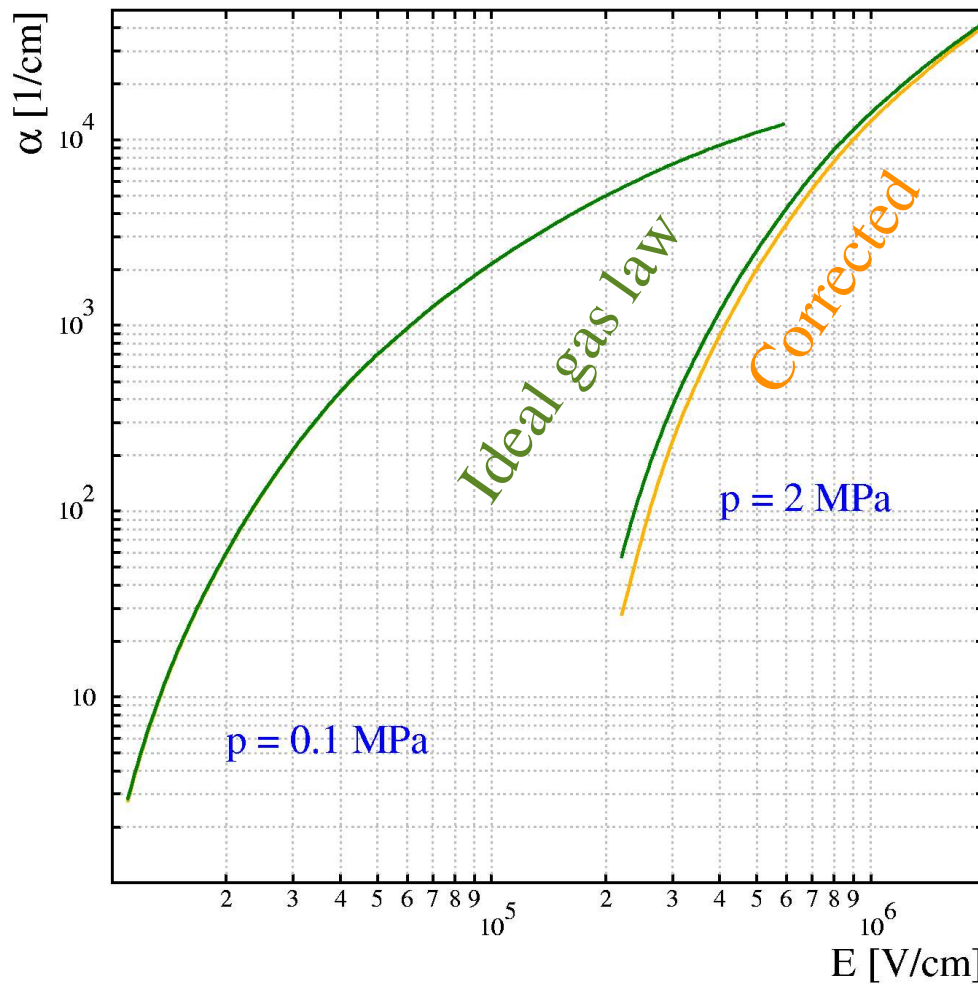
$$N^{\text{true}} = N^{\text{ideal}} / Z$$

- ▶ Through the scaling law for Townsend coefficients, the corrected Townsend coefficient is related to the ideal gas law values at a scaled electric field E :

$$\frac{\alpha(E, N)}{N} = f\left(\frac{E}{N}\right), \quad \alpha\left(E, \frac{N^{\text{ideal}}}{Z}\right) = \frac{\alpha(E Z, N^{\text{ideal}})}{Z}$$

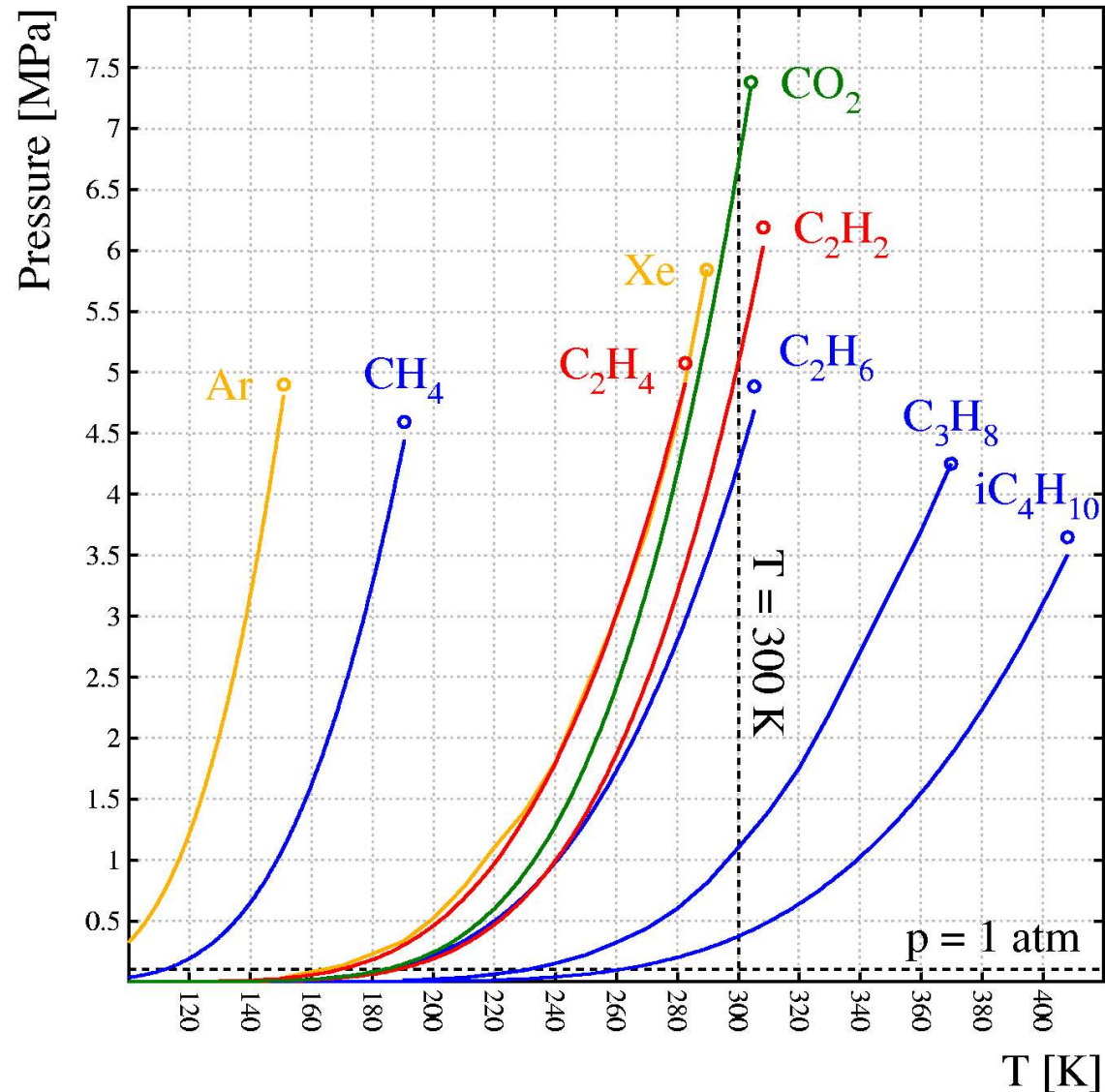
Example

- ▶ Xe 90 % CH₄ 10 %: the corrected gain is *lower*.



Vapour pressure

- ▶ Conceivably, some of the measurements can have been affected by condensation.
- ▶ Except for Xe- iC_4H_{10} and Xe- C_3H_8 , this can be ruled out.
- ▶ Note: vapour pressure curves are approximate (Antoine's law).



What we have learned

- ▶ The measured gas gain in Xe mixtures is consistently higher than calculated, even in non-Penning mixtures.
- ▶ The ionisation cross section has been improved at threshold, but this does not solve the problem.
- ▶ Associative ionisation may be part of the reason, but further work is needed on the excitation cross sections.
- ▶ Virial corrections make the problem worse.
- ▶ Steve Biagi will present further ideas in a forthcoming meeting.