

# Write-up of the Speed of Sound in CO<sub>2</sub>-Inert Mixtures

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## 1. Introduction [1]

### 1.1 Laplace formula and its assumption

$$W_s^2 = \frac{\gamma_s RT}{M} \quad (1.1)$$

where  $\gamma_s = 5/3$  for a monoatomic gas

$$= 7/5 \quad \text{for a diatomic gas or linear polyatomic gas} \quad (1.2)$$

$$= 4/3 \quad \text{for a nonlinear polyatomic gas}$$

Here  $W_s$  is the speed of sound,  $\gamma_s$  the ratio of specific heats  $C_p/C_v$  at constant pressure and constant volume, R the universal gas constant, and M the molar mass. Equations (1.1) and (1.2) are based on three assumptions:

1. The molecular rotational degrees of freedom are fully excited and vibrational degrees of freedom are fully unexcited. There are no other internal contributions to the specific heat.
2. The state of the gas is governed by the ideal gas law:

$$P = \rho RT$$

3. Propagation through the gas is lossless.

### 1.2 Corrections to the laplace formula

The corrections required to compensate for violations of the preceding three assumptions are called the specific heat, virial, and relaxation corrections. Quantities related to these corrections are denoted by subscripts c, v, and r, respectively. The speed of sound of a real gas is written accordingly:

$$W^2 = \frac{\gamma_s RT}{M} (1 + K_c)(1 + K_v)(1 + K_r) \quad (1.3)$$

where  $K_c$ ,  $K_v$ , and  $K_r$  are the specific heat, virial, and relaxation corrections.

## 2 Details on corrections

### 2.1. specific heat correction

i)  $K_c$  or  $(\gamma_0 = \gamma_s(1 + K_c))$  is only a function of temperature.

$$K_c(T)$$

ii) calculation [2]

$$W^2 = \frac{\gamma_s RT}{M} (1 + K_c) = \frac{RT}{M} \gamma_0 \quad (2.1.1)$$

$$\gamma_0(T) = \frac{C_p^0}{C_v^0} = \frac{C_p^0}{C_p^0 - R} = \frac{C_p^0 / R - 1 + 1}{C_p^0 / R - 1} = 1 + (C_p^0 / R - 1)^{-1} \quad (2.1.2)$$

$C_p^0$  can be represented by the following polynomial in temperature T:

$$C_p^0 / R = a_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_{-1} T^{-1} \quad (2.1.3)$$

Therefore, the specific heat correction can be calculated as:

$$K_c(T) = (\gamma_0 / \gamma_s) - 1 \quad (2.1.4)$$

which is only a function of T.

Values of  $\gamma_s$  and coefficients of equation (2.1.2) for different gases can be found in [3].

Gas	$\gamma_s$	$a_0$	$a_1 \times 10^{-3}$	$a_2 \times 10^{-6}$	$a_3 \times 10^{-9}$	$a^{-1} \times 10^{-9}$	Temp. range (K)
Ar	5/3	1.5	0	0	0	0	10 – 6000
Xe	5/3	1.5	0	0	0	0	10 – 5200
CO2	7/5	1.3457	8.9374	-6.7157	1.8369	0	200 - 590

Table 2.1 Simple Specific Heat Ratios, Coefficients of Eq. (2.3.1) and the Temperature Range of Validity

## 2.2 *virial correction*

i)  $K_v$  is a function of temperature and pressure

$$K_v(T, P)$$

ii) The virial equation of state is chosen to represent the nonideality of the gas. Only the first three terms will be retained in the virial expansion, namely the constant, the terms containing the second coefficient B and terms containing the third coefficient C, since at extremely high pressure where the fourth coefficient term would become prominent, the state of a gas cannot be represented adequately by a power series expansion. This is especially true at pressures exceeding the critical pressure.

iii) calculation [4]

The virial correction is based on a three-parameter formula by Kaye and Laby for the second virial coefficient and a new five-parameter empirical formula for the third virial coefficient.

$$W^2 = \frac{\gamma_0 RT}{M} \left( 1 + \frac{K}{V} + \frac{L}{V^2} \right) \quad (2.2.1)$$

The second virial coefficient (three parameters:  $a_v$ ,  $b_v$ ,  $c_v$ ):

$$K = a_v(0) + \left[ a_v(1) + \frac{a_v(2)}{T} + \frac{a_v(3)}{T^2} \right] \exp(C_v/T) \quad (2.2.2)$$

in which  $a_v(i)$ ,  $i=0$  to  $3$ , is functions of the three parameters  $a_v$ ,  $b_v$ , and  $c_v$ .

The third virial coefficient ( $a_v, b_v$ , and  $c_v$  + 5 parameters:  $d_v, e_v, f_v, g_v$ , and  $c_\infty$ ):

$$L = [a_w(0) + a_w(1)\exp(c_v/T) + a_w(2)T^{-2}\exp(c_v/T)]^2 + [a_w(3) + a_w(4)T + a_w(5)T^2]\exp(-g_v/T) + [a_w(6) + a_w(7)T^{-1} + a_w(8)T + a_w(9)T^{-2} + a_w(10)T^2]\exp(f_v/T - g_v/T) + a_w(11) \quad (2.2.3)$$

in which  $a_w(i)$ ,  $i=0$  to  $11$ , are functions of  $a_v, b_v, c_v, d_v, e_v, f_v, g_v$ , and  $c_\infty$ .

Expressions for  $a_v$  can be found in [5].

Expressions for  $a_w$  can be found in [6].

Values for parameters  $a_v, b_v, c_v, d_v, e_v, f_v, g_v$ , and  $c_\infty$  can be found in [7].

Gas	$a_v(\text{cm}^3/\text{mol})$	$b_v(\text{cm}^3/\text{mol})$	$c_v(\text{K})$	Temperature range (K)
Ar	154.2	119.3	105.1	80 – 1300
Xe	245.6	190.9	200.2	160 – 650
CO2	137.6	87.7	325.7	220-1100

Table 2.2 (a)

Gas	$d_v(\text{cm}^3/\text{mol})^2$	$e_v(\text{cm}^3/\text{mol})^2$	$f_v(\text{K})$	$g_v(\text{K}^{-1})$	$c_\infty(\text{cm}^3/\text{mol})$	T range (K)
Ar	13439.72	2304.823	146.346 4	0.01	761.25	80 – 1223
Xe	58442.23	602.336	992.313	0.008	1829.25	209 - 573
CO2	113548.2	83.43604	1581.72 5	0.011	1556.2	230 - 773

Table 2.2 (b)

Table 2.2 Constants of the Second & Third Virial Coefficients and Temperature Range of Validity

### 2.3 Relaxation correction

i)  $K_r$  is a function of temperature( $T$ ), pressure( $P$ ), and frequency( $\omega$ ).

$$K(T, P, \omega)$$

a) A relaxation process is characterized by two parameters: a relaxation strength  $\varepsilon(T)$  and a relaxation time  $\tau(T, P)$ .

b) The frequency dependence of the relaxation correction is inherent in the nature of the relaxation equations.

ii) calculation [8]

$$W^2 = W_\theta^2 \left[ 1 + \frac{\varepsilon}{1 - \varepsilon} \frac{(\omega\tau)^2}{1 + (\omega\tau)^2} \right] \quad (2.3.1)$$

Note:  $\tau$  here is the relaxation time for the sound dispersion.

$W_\theta$  is the sound speed in the limit to zero frequency, containing the specific heat and virial corrections.

Thus, the relaxation correction is:

$$K_r = \frac{\varepsilon}{1 - \varepsilon} \frac{(\omega\tau)^2}{1 + (\omega\tau)^2} \quad (2.3.2)$$

$\varepsilon(T)$  can be calculated as:

$$\varepsilon = 1 - \frac{W_\theta^2}{W_\infty^2} = \frac{RC_i}{(C_p^0 - C_i)(C_p^0 - R)} \quad (2.3.3)$$

in which  $W_\theta$  is the sound speed in the zero frequency limit, and  $W_\infty$  is the sound speed in the infinite frequency limit.  $C_i = C_v^\theta - C_v^\infty$  is the difference between a low-frequency and high-frequency specific heat, just the specific heat of the relaxing degrees of freedom.

$C_i$  is given by:

$$C_i = R \quad \text{or} \quad C_i = \frac{3}{2}R, \quad (2.3.4)$$

for the rotational degrees of freedom of linear and nonlinear molecules, respectively.

$$C_i = q_i R \left( \frac{\theta_{vb}^{(i)}}{T} \right)^2 \frac{\exp\left(-\frac{\theta_{vb}^{(i)}}{T}\right)}{\left[1 - \exp\left(-\frac{\theta_{vb}^{(i)}}{T}\right)\right]^2} \quad (2.3.5)$$

for the  $i$ th mode of the vibrational degrees of freedom.

$\tau(T, P)$  can be calculated as:

$$\log(\tau P) = a_r(1) + a_r(2)T^{-1/3} + a_r(3)T^{-1} \quad (2.3.6)$$

$\tau$  in  $\mu$  s, and  $P$  in atm.

$T^{-1/3}$  ----- Landau-Teller temperature dependence

$T^{-1}$  ----- Arrhenius temperature dependence

Values of parameters  $a_r(1)$ ,  $a_r(2)$ , and  $a_r(3)$  can be found in [9].

### 3 Mixing rules

In our case, we are interested in the mixing rules for CO<sub>2</sub> – monoatomic gas (like Ar, Xe), so we focus on this. Actually, the fact that one component of the mixture is monoatomic gas will make our

life much easier, because monoatomic gases don't have specific heat and relaxation correction since they don't have vibrational freedoms.

Denote the fraction of CO2 to be  $x$ , the mass of monoatomic gas to be  $M_{mono}$ .

### 3.1 Molar Mass

$$M_{mix} = \sum x_i M_i = x M_{co2} + (1-x) M_{mono} \quad (3.1.1)$$

Molecule	Molar Mass ( g / mol )
Ar	39.9478
Xe	131.29
CO2	44.010

Table 3.1 Molar Mass of Selected Molecules

### 3.2 Specific heat correction [10]

$$\begin{aligned} \frac{C_{pmix}^0}{R} &= \frac{1}{R} [x C_{pco2}^0 + (1-x) C_{pmono}^0] = x \sum_n a_{n\_co2} T^n + (1-x) \sum_n a_{n\_mono} T^n \\ &= x \sum_n (a_{n\_co2} - a_{n\_mono}) T^n + \sum_n a_{n\_mono} T^n \end{aligned} \quad (3.2.1)$$

denote  $A = \sum_n (a_{n\_co2} - a_{n\_mono}) T^n$ ,  $B = \sum_n a_{n\_mono} T^n$ , then we get:

$$\gamma_{0mix} = \gamma_{smix} (1 + K_c) = 1 + (Ax + B - 1)^{-1} \quad (3.2.2)$$

### 3.3 Virial correction

The second virial coefficient:

$$K_{mix} = x^2 K_{11} + 2x(1-x)K_{12} + (1-x)^2 K_{22} \quad (3.3.1)$$

in which  $K_{11}$  and  $K_{22}$  are the second virial coefficients of pure components,  $K_{12}$  is the interaction of them.  $K_{12} = E + (K_{11} + K_{22})/2$ .  $E$  is the excess second virial coefficient at the specific temperature for the mixture [11]. This term can often be ignored [12].

The third virial coefficient:

$$L_{mix} = x^3 L_{111} + 3x^2(1-x)L_{112} + 3x(1-x)^2 L_{122} + (1-x)^3 L_{222} \quad (3.3.2)$$

in which  $L_{111}$  and  $L_{222}$  are the third virial coefficients of pure components,  $L_{112} = (L_{111}^2 L_{222})^{1/3}$ ,

$$L_{122} = (L_{111} L_{222}^2)^{1/3}.$$

### 3.4 Relaxation correction [13]

Only CO2 has relaxation correction. In such a mixture,  $\varepsilon$  for CO2 can be calculated as:

$$\varepsilon = \frac{RxC_{ico2}}{(C_{pmix}^0 - xC_{ico2}^0)(C_{pmix}^0 - R)} \quad (3.4.1)$$

with

$$C_{pmix}^0 = xC_{pco2}^0 + (1-x)C_{pmono}^0, \quad \text{where } C_{pco2}^0 \text{ and } C_{pmono}^0 \text{ are approximately to be } \frac{7}{2}R$$

and  $\frac{3}{2}R$ , respectively.

$$C_{ico2} = R\left(\frac{\theta_{vb}}{T}\right)^2 \frac{\exp\left(-\frac{\theta_{vb}}{T}\right)}{\left[1 - \exp\left(-\frac{\theta_{vb}}{T}\right)\right]^2} \quad \text{where } \theta_{vb} \text{ for CO2 is 959.7K.}$$

Note:  $\varepsilon$  is much smaller than unity,  $\varepsilon \ll 1$ . Just give a flavor of the magnitude of  $\varepsilon$ , at

$$T=371.15K, P=0.9671atm, W_{\theta}=298.2 \text{ m/s}, W_{\infty}=313.5 \text{ m/s [14], } \varepsilon=0.1.$$

$\tau$  for CO2 in a CO2-monoatomic (eg. Ar) mixture can be calculated as [8][15][17]:

$$\frac{1}{\tau} = \frac{x}{\tau_{co2}} + \frac{1-x}{\tau_{co2-Ar}} \quad (3.4.2)$$

$\tau_{co2}$ : relaxation time of one CO2 molecule in pure CO2 gas;

$\tau_{co2\_Ar}$ : relaxation time of ONE CO2 molecule in an otherwise PURE Ar gas.

From the equation (2.3.1), we can see that:

- 1) The maximum of relaxation correction is  $\frac{\varepsilon}{1-\varepsilon}$ ,

$$K_{r \max} \leq \frac{\varepsilon}{1-\varepsilon}$$

- 2) If the relaxation time is much smaller than the period of the sound wave,  $\tau \ll 1/\omega$ , then

$$\frac{(\omega\tau)^2}{1+(\omega\tau)^2} \rightarrow 0, \text{ that is the relaxation correction will be very small, so that can be ignored.}$$

$\tau_{co2} = 3.6 \pm 0.2 \mu s$  at 1 atm, 293K [16];

$\tau_{co2\_Ar} \sim 30 \mu s$  at 1 atm, room temperature [17].

Since  $\tau_{co2\_Ar} > \tau_{co2}$ , adding some monoatomic molecules will increase the relaxation time of CO2 molecule. However,  $\tau$  changes with temperature. We have seen before that  $\tau_{co2}$  has a  $T^{-1/3}$  dependence. Some studies [17] show that  $\tau_{co2\_Ar}$  also has such similar  $T^{-1/3}$  dependence. Values of the parameters in (2.3.5) for  $\tau_{co2}$  can be found in [9], however, it's not easy to find values of the parameters for  $\tau_{co2\_Ar}$ . I use data from [17] to get those parameters for  $\tau_{co2\_Ar}$  in my calculation (table 3.4). More details for the theory of the calculation of vibrational relaxation times can be found in [8][15][18].

## 4 Some flavor of how big these corrections are

### 4.1 *specific heat*

See Fig 1.

### 4.2 *virial*

This correction will increase dramatically with pressure. Fortunately, our experiment is done under about 1 atm, and not very high pressure. In this condition, virial correction is unimportant, usually at least one order smaller than the specific heat correction.

### 4.3 *relaxation*

This correction will increase with frequency, Fig 2. Fortunately, we can know its maximum value, from Fig 2, we can see that when the frequency is high enough,  $K_r$  is just equal to  $K_{r,max}$ . The frequency of the sound wave of the spirometer we are using is 50kHz, whose period is  $20 \mu s$ , and the relaxation time of CO2 in a CO2-Ar mixture is right of the same order, so if we want to calculate this correction accurately, we have to deal with the complicated relaxation time calculation in mixtures, which is not very well known. Fig 3 shows how  $K_r$  of different mixtures changes with temperature at 1 atm with such a frequency. (How I estimate  $\tau_{co2\_Ar}$  was mentioned in 3.4.

The lowest frequency of sound wave our spirometer [19] can generate is 10kHz, whose period is  $100 \mu s$ , is still not low enough to ignore  $K_r$ . A good thought to simplify problem might be to generate a very high frequency, so that we can use  $K_{r,max}$ , instead of  $K_r$ . The advantage of doing this is to avoid dealing with relaxation time. The highest frequency our spirometer can generate is 2.5MHz, which is high enough.

Fig 4 shows corrections of specific heat together with those of the relaxation.

## 4.4

Fig 5 is the theoretical and data curves of transit time vs temperature of mixtures with different CO2 concentrations.

It can be seemed that, 1% change of CO2 can only result in 0.2% change in transit time, so thus sound speed. Therefore, in order to attain 1% accuracy in CO2 concentration measurement, specific heat and relaxation correction need to be considered.

## 5 Some thoughts of how to apply it in real life

Fig 6 is a series of theoretical curves of transit time vs CO2 concentration, at 1 atm, a certain temperature not far from room temperature, with 50kHz, including specific heat and relaxation corrections.

It can be seemed that quadratic fit is already good enough.

$$tt(T) = a_0(T) + a_1(T)x + a_2(T)x^2 \quad (5.1)$$

Fig 7 shows how it works with our data. We can see that with a suitable recalibration, we can measure the CO2 concentration in the temperature range 15C-25C up to the accuracy about 2%.

We still need to check further to see whether equation (5.1) works well. If it works, in practice, we can measure transit time vs temperature of three mixtures, say CO2:Ar=0:100, CO2:Ar=20:80, and CO2:Ar=100:0, then get a table of  $a_0$ ,  $a_1$ , and  $a_2$  in different temperatures. Therefore,

given a mixture with unknown CO2 concentration, if its transit time is  $tt$  at  $T_0$ , we can look up values for parameters  $a_0(T_0)$ ,  $a_1(T_0)$ , and  $a_2(T_0)$  in the lookup table and solve the equation (5.1), to get the concentration of CO2.

Note: All C codes can be found at <http://web.mit.edu/saxiao/Public/SoundSpeed/scr/>

References:

- [1] Allan J. Zuckerwar, *Hand book of the Speed of Sound in Real Gas*, Academic Press, 2002
- [2] Zuckerwar, *ibid.*, chapter 3
- [3] *op. cit.*, Table3.1
- [4] *op. cit.*, chapter 4
- [5] *op. cit.*, page 95
- [6] *op. cit.*, page 103
- [7] *op. cit.*, Table4.1 & 4.2
- [8] *op. cit.*, chapter 5
- [9] *op. cit.*, Table5.5
- [10] *op. cit.*, chapter 16.4.3
- [11] Turk. J. Chem., 26, 2002
- [12] Zuckerwar, *ibid.*, chapter 16.4.4
- [13] *op. cit.*, chapter 16.4.5
- [14] *op. cit.*, chapter 9.2
- [15] J.R.Olson, J. Chem. Phys., Vol 39, No.11, 1963
- [16] J. Phys. B, 1968, Sept. 2, Vol 1
- [17] J. Chem. Phys., Vol51, No.5, Sept. 1, 1969
- [18] R. N. Schwartz, Z. I. Slawsky, K.F. Herzfeld, J. Chem. Phys., Vol 20, No. 10, Oct., 1952
- [19] Specification nnd ASIC A1 – A4, nnd Medizintechnik, Zurich, 2003

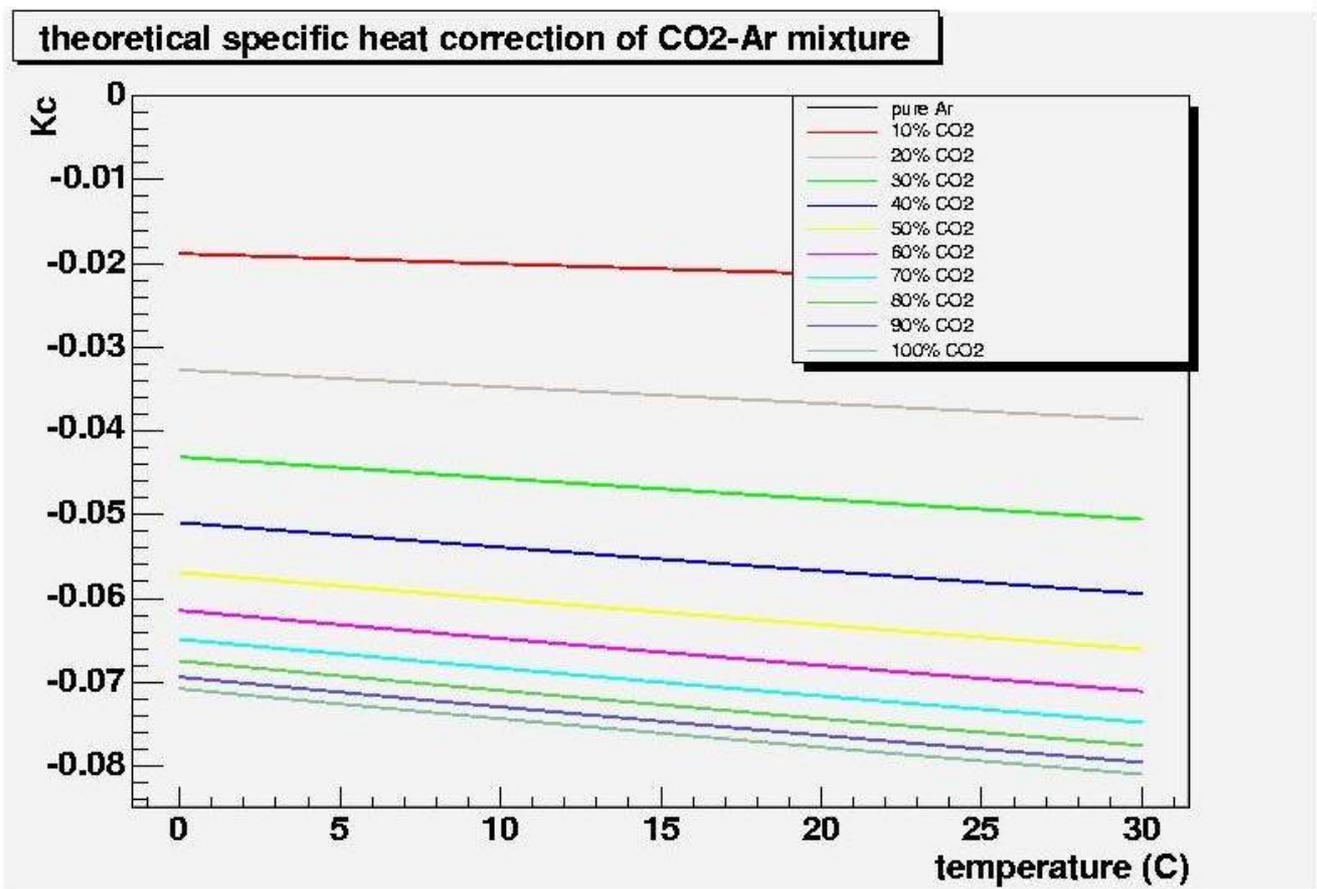


Fig 1 Theoretical curve of specific heat correction vs temperature of different CO<sub>2</sub> – Ar mixtures at about 1 atm.  $K_c$  is calculated by eq. (3.2.2).

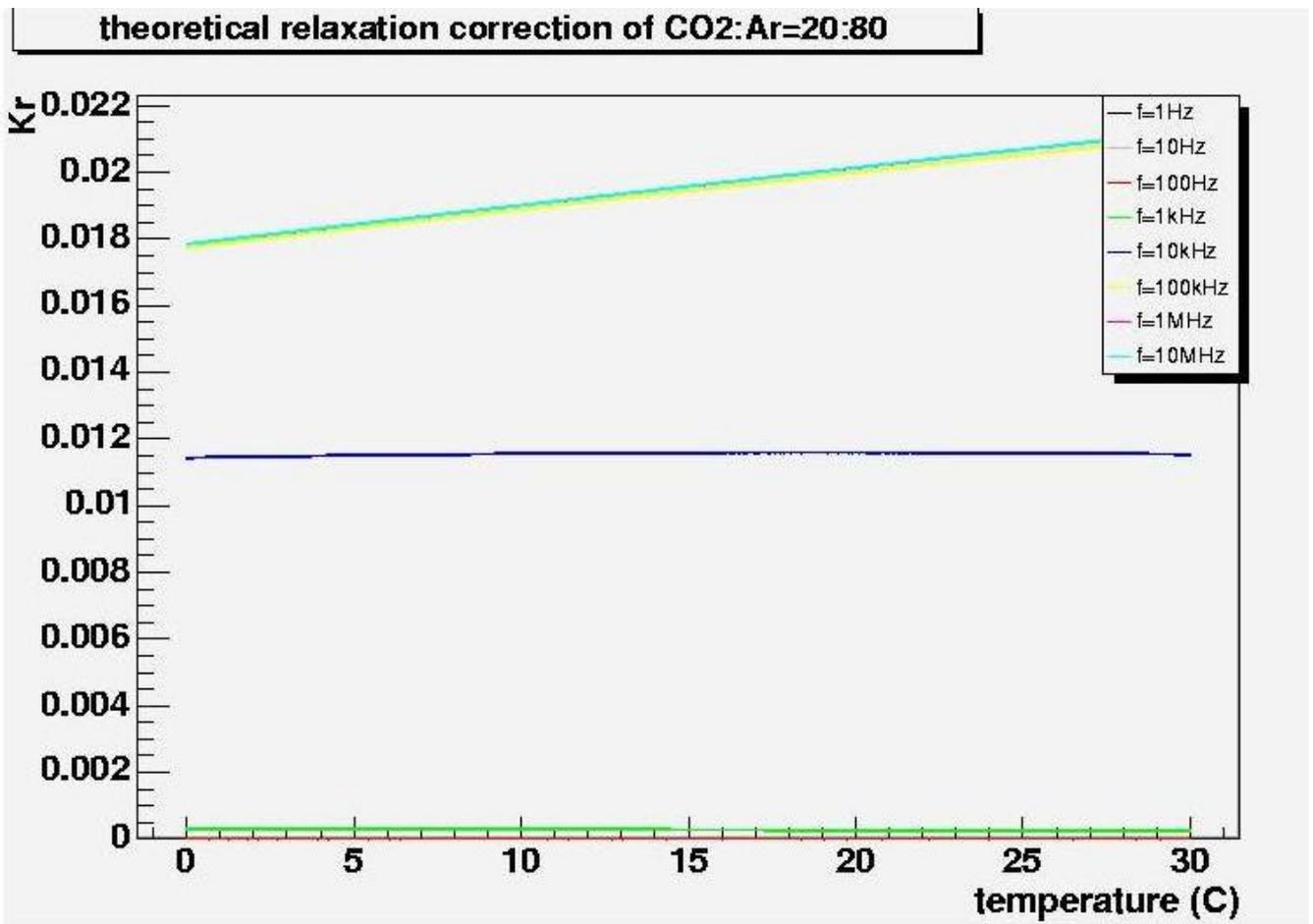


Fig2, when frequency is low, the correction is very small, it is almost zero until attaining 1kHz, the green line at the bottom. The correction increases as frequency increases, and attenuates at some point. So the correction attain a maximum value when the frequency is high enough, you can hardly tell the differences between the last three curves. The yellow, purple, and light blue ones at the top.

theoretical relaxation correction of CO<sub>2</sub>-Ar mixture at 1 atm, 50kHz

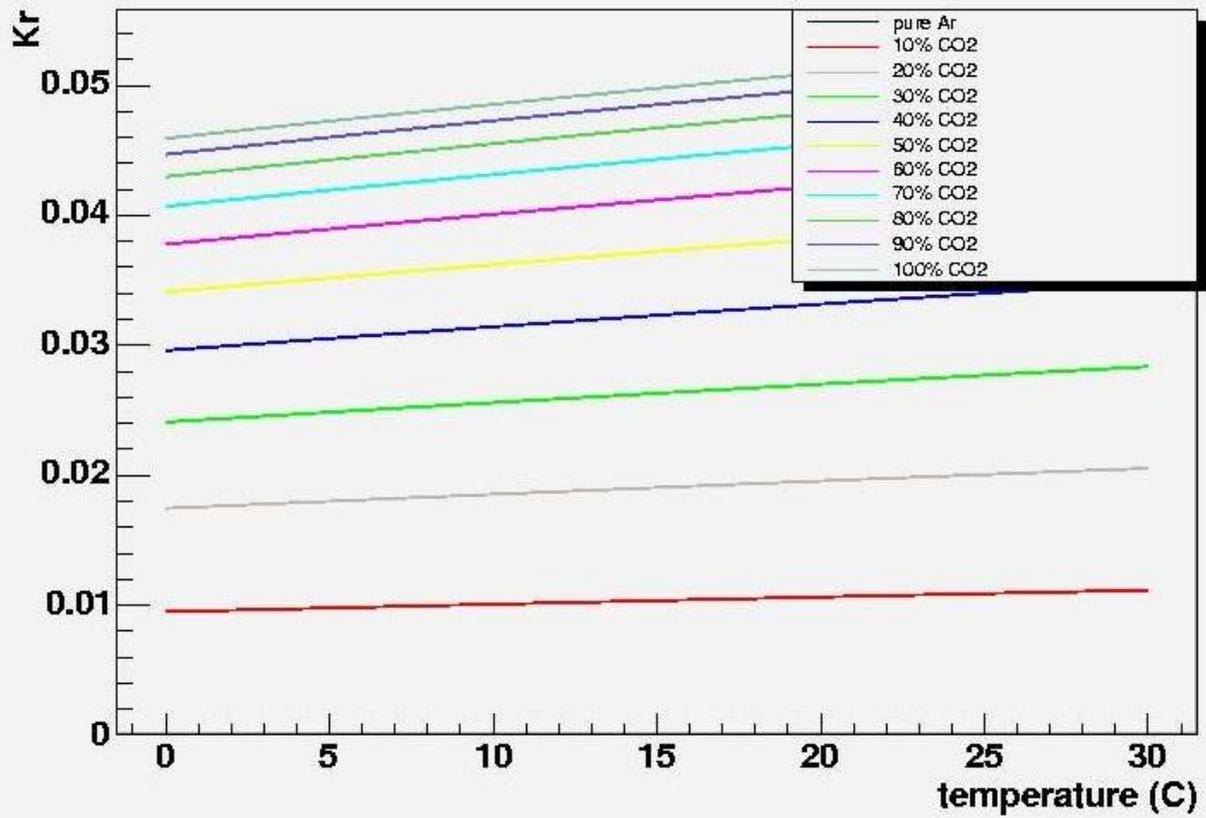


Fig 3 Theoretical curve of relaxation correction vs temperature of different CO<sub>2</sub> – Ar mixtures at 1 atm, 50 kHz.  $K_r$  is calculated by Eq. (2.3.2), together with eq. (3.4.1), eq. (3.4.2), eq. (2.3.6).

theoretical correction of CO<sub>2</sub>-Ar mixture at 1atm, 50kHz (specific heat & relaxation)

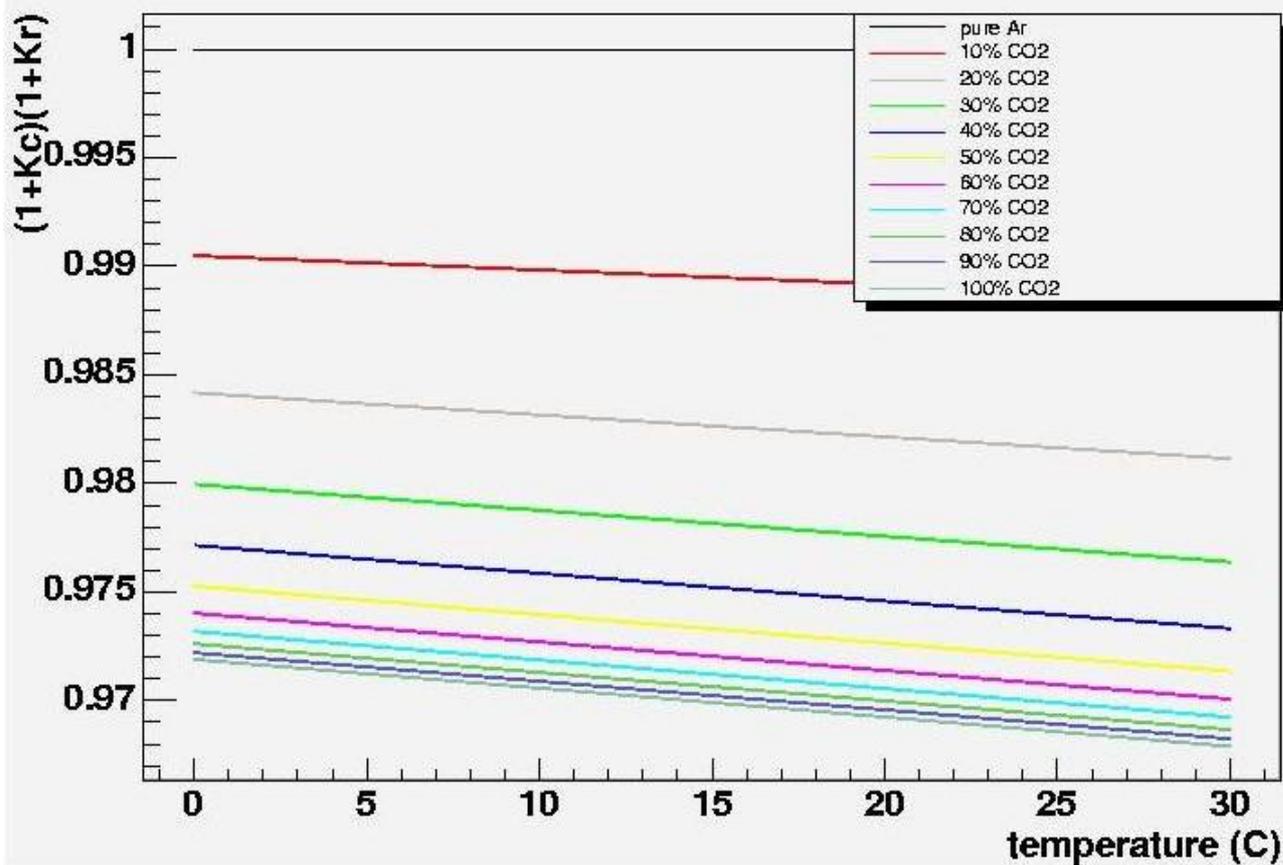


Fig 4 Theoretical curve of combined specific heat and relaxation correction vs temperature, at 1 atm, 50 kHz. It can be seen that, there is no correction for pure Ar (in such condition, virial correction can be ignored), and the correction increases as CO<sub>2</sub> concentration increases.

### Ar-CO2 Transi time vs Temp with different CO2 concentration

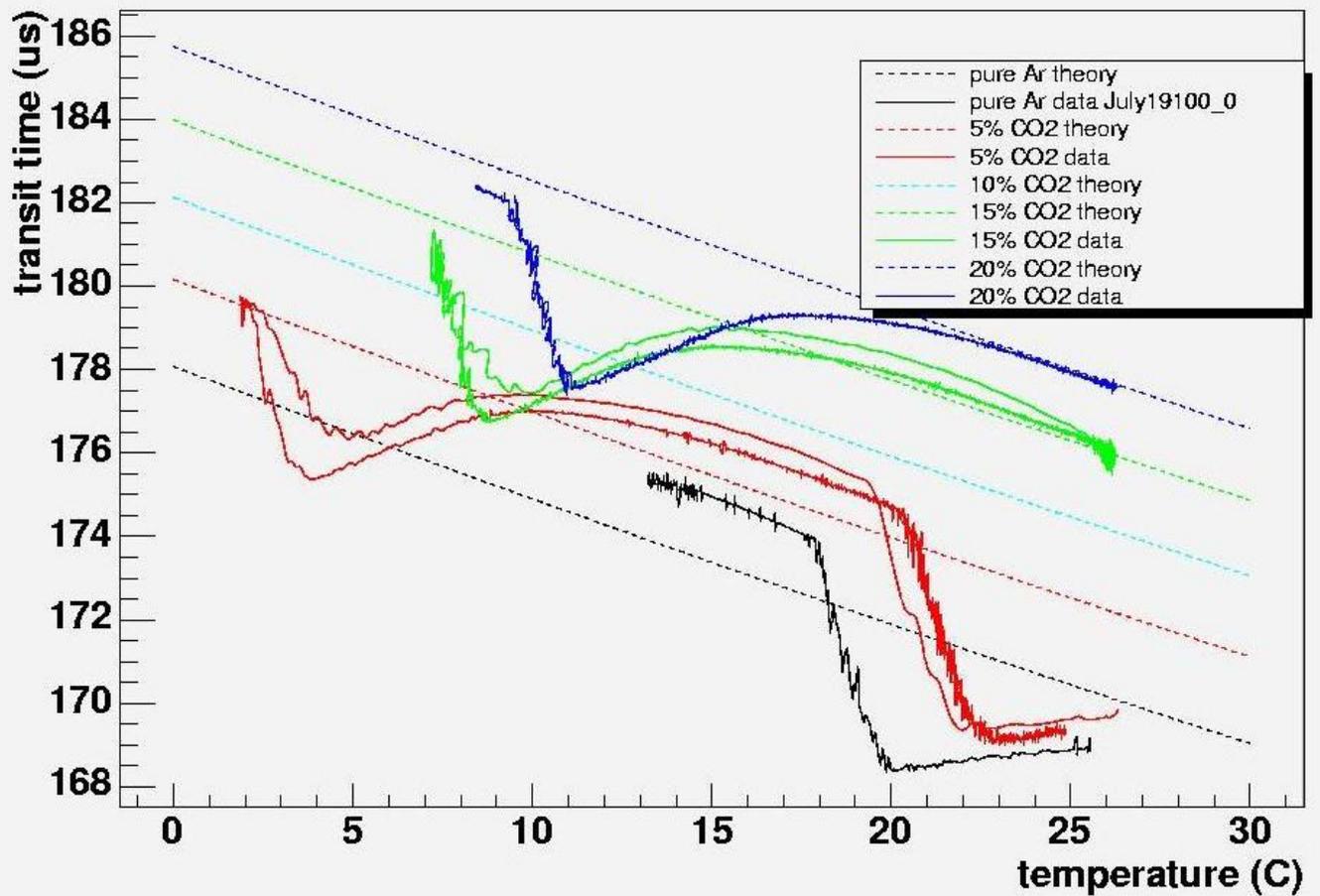


Fig 5 The solid lines are data, taking by Daniel Chonde, and the dashed lines are theoretical curves, calculated by eq. [1.3], including specific and relaxation corrections.

theoretical of transit time vs CO2 concentration of CO2-Ar mixtures

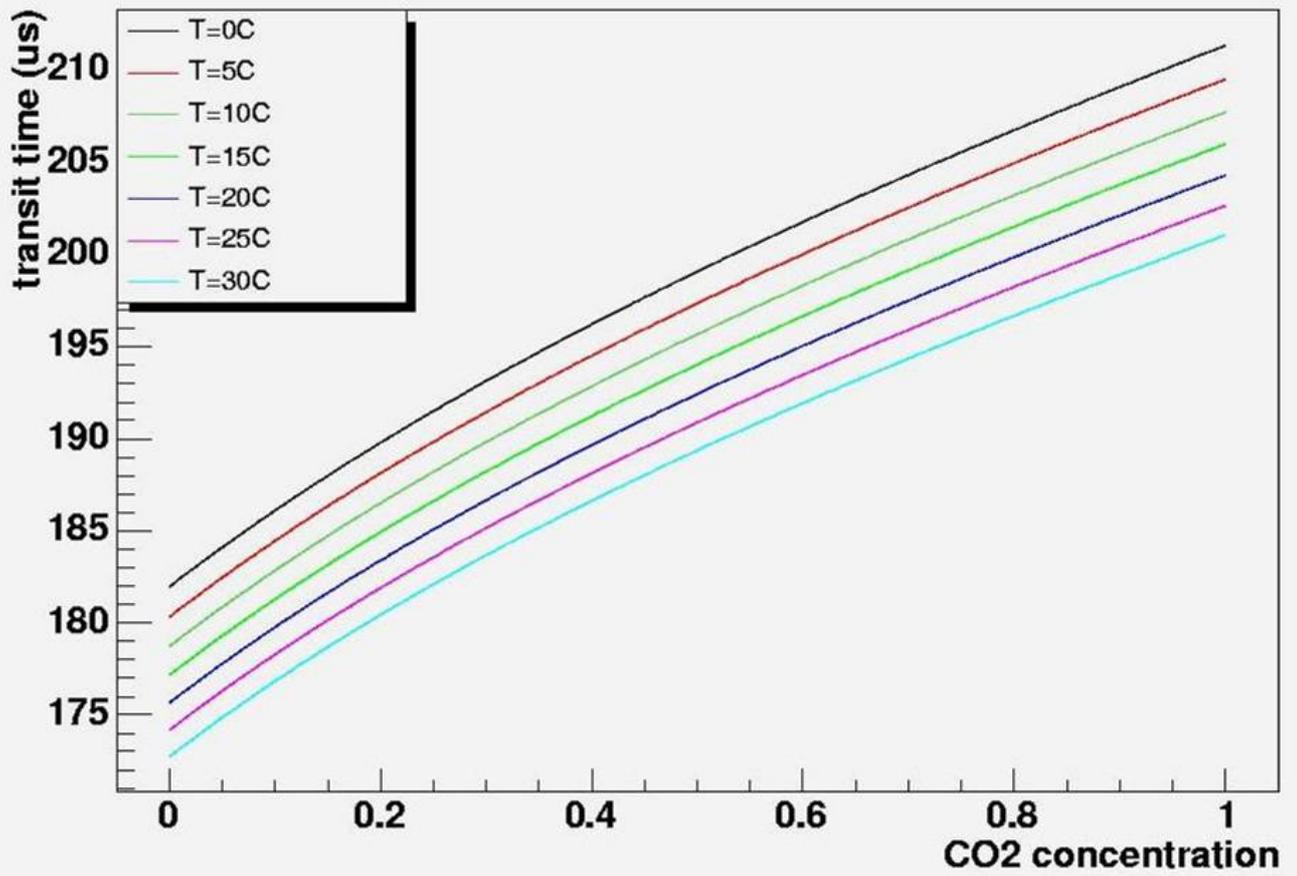


Fig 6 Theoretical curves of transit time vs CO2 concentration of different CO2 – Ar mixtures, at 1 atm, and different temperatures.

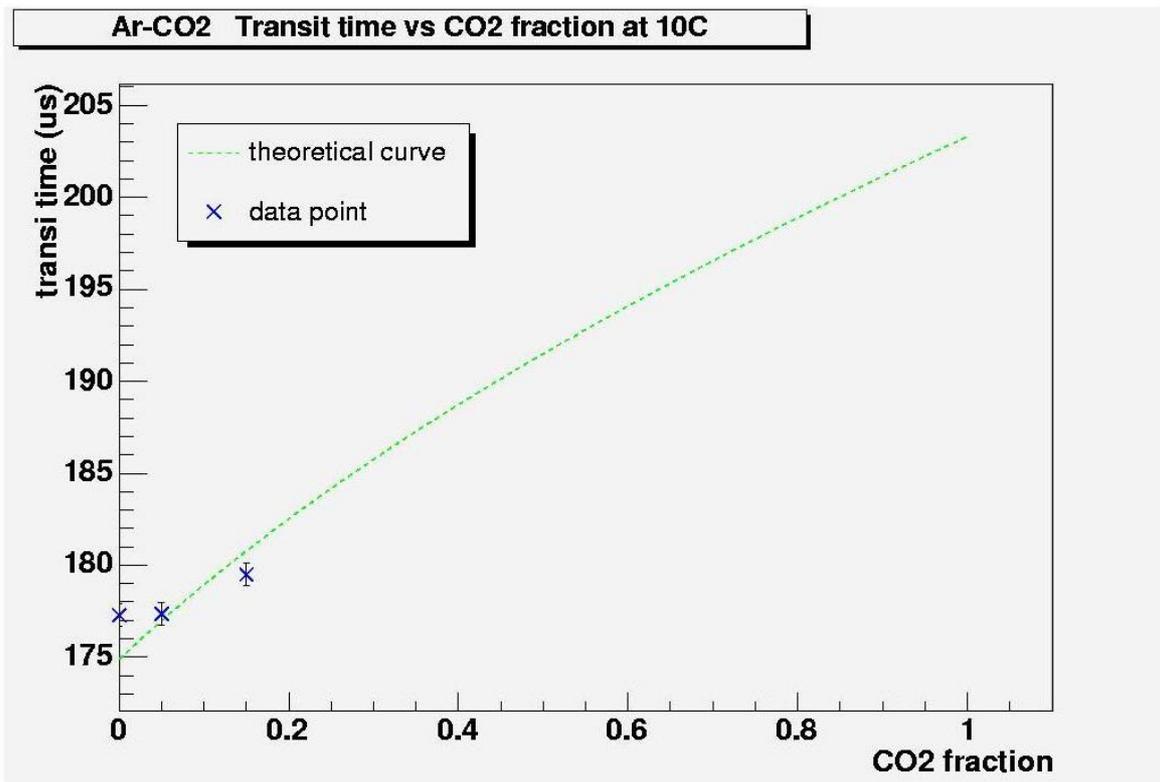


Fig 7 (a) Solid curve is theory, and the dots are data taken by Daniel Chonde.

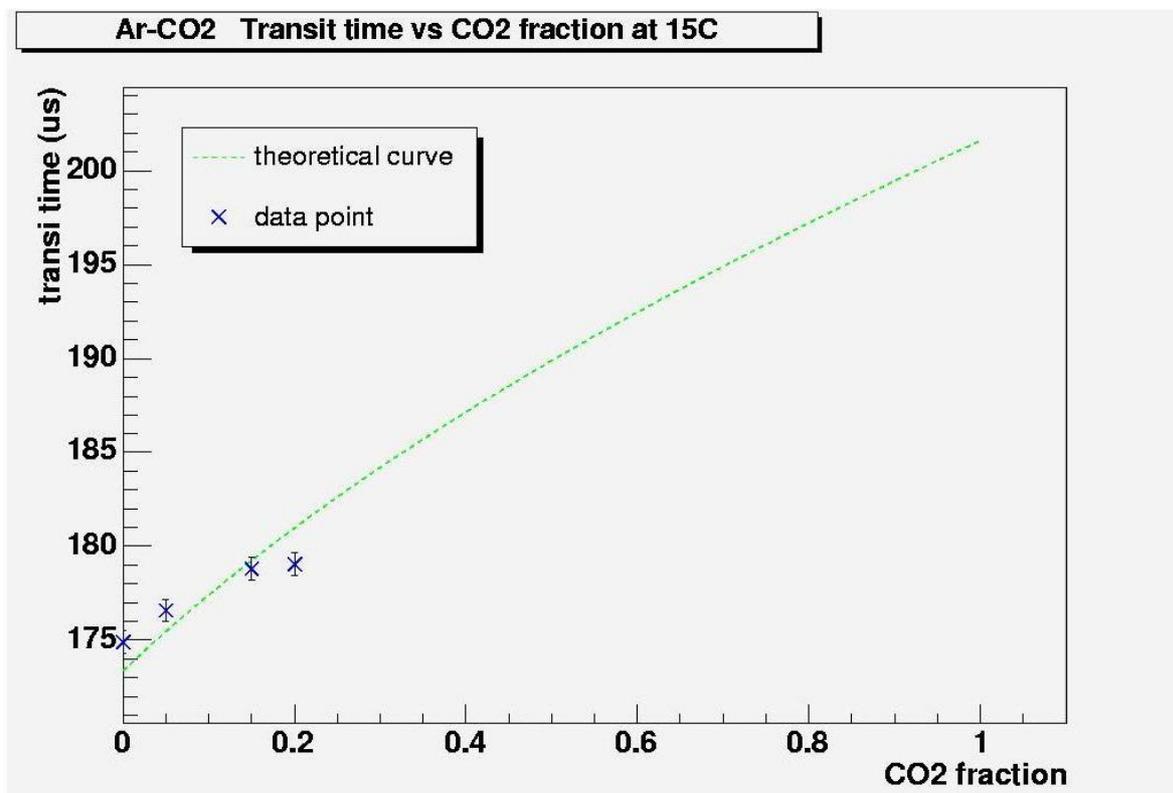


Fig 7 (b) Solid curve is theory, and the dots are data taken by Daniel Chonde.

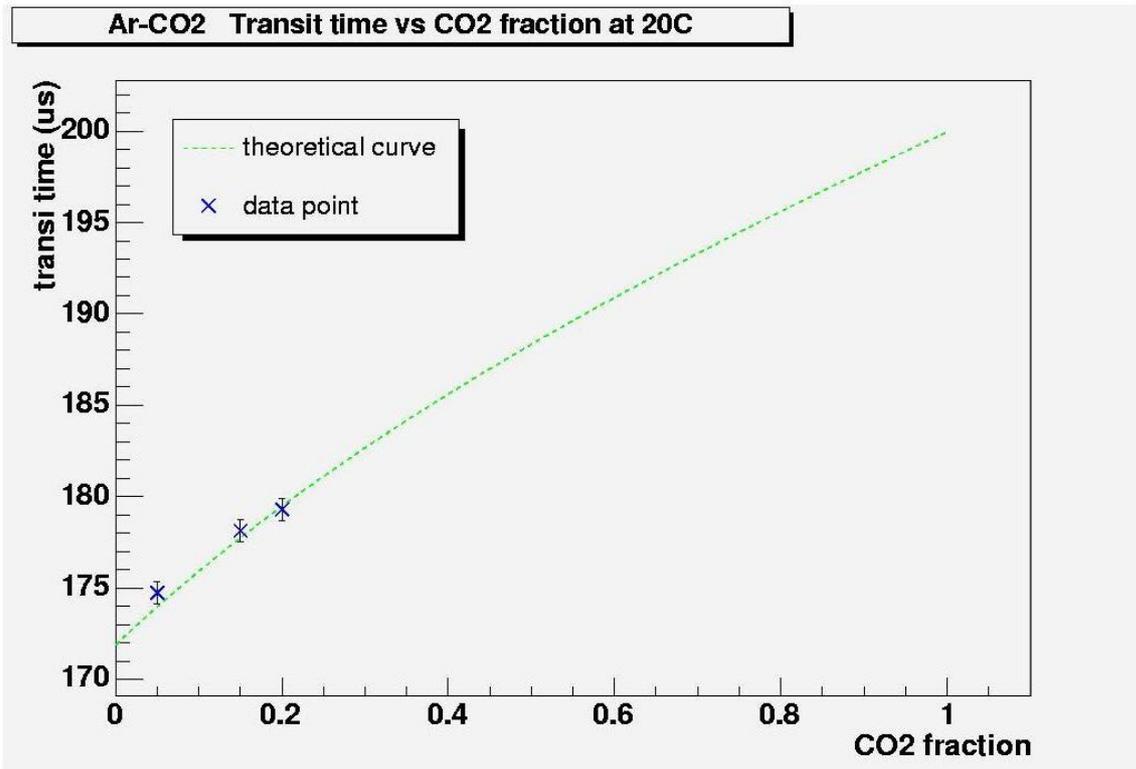


Fig 7 (c) Solid curve is theory, and the dots are data taken by Daniel Chonde.

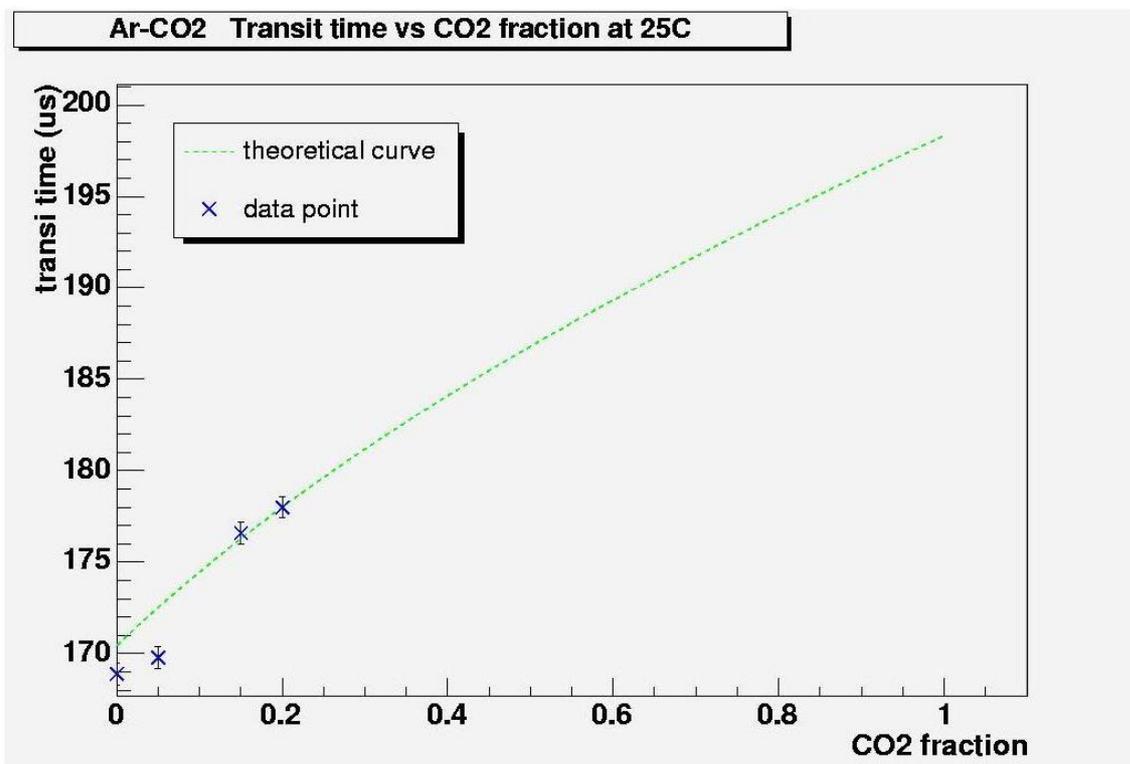


Fig 7 (d) Solid curve is theory, and the dots are data taken by Daniel Chonde.

## Appendix A C Code for Calculating Specific Heat & Relaxation Corrections

```

#include <iostream>
#include <fstream>
#include <TGraph>

#define N 6000
#define N1 11
#define step 0.005
#define T_min 273.15

float R=8.31;
float a_xe[5]= {2.5,0.,0.,0.,0.};
float a_ar[5]= {2.5,0.,0.,0.,0.};
float a_co2[5]= {2.3457,8.9374e-3,-6.7157e-6,1.8369e-9,0.};
float a1_co2=-1.25,a2_co2=14, a1_CO2inAr=-1.46, a2_CO2inAr=19.5;
float m_xe=131.29e-3, m_ar=39.9478e-3,m_co2=44.010e-3; //molar mass in kg/mol
float Tv_co2=959.7;
float m_co2=44.010e-3;
float L=0.0548; //unit m

float K_sp(float T_in, float x_co2) //calculate specific heat correction{

float gamma_s, gamma_c,temp=0, Kc,gamma_s=(x_co2*7+(1-x_co2)*5)/(x_co2*5+(1-x_co2)*3);
for(int j=0; j<4;j++)
temp=temp+x_co2*a_co2[j]*pow(T_in,j)+(1-x_co2)*a_ar[j]*pow(T_in,j);
temp=temp-1;
gamma_c=1+1/temp;
Kc=gamma_c/gamma_s-1;
return Kc; }

float K_re(float T_in, float freq, float x_co2) //relaxation correction

{ float t_re_mix, t_re_co2,t_re_CO2inAr,temp,t_re_mix_SI,C_i,epsno,Kr_max,Kr;
float C_s=x_co2*3.5*R+(1-x_co2)*2.5*R;

//calculate relaxation time
temp=a1_co2+a2_co2*pow(T_in,-0.333);
t_re_co2=pow(10,temp);
temp=a1_CO2inAr+a2_CO2inAr*pow(T_in,-0.333);
t_re_CO2inAr=pow(10,temp);
t_re_mix=1/(x_co2/t_re_co2+(1-x_co2)/t_re_CO2inAr); //in us
t_re_mix_SI=t_re_mix*1e-6;

//calculate epsno
temp=Tv_co2/T_in;
C_i=R*temp*temp*exp(-temp)/pow((1-exp(-temp)),2);
epsno=x_co2*R*C_i/(C_s-x_co2*C_i)/(C_s-R);
temp=freq*freq*t_re_mix_SI*t_re_mix_SI;
r_max=epsno/(1-epsno);
Kr=Kr_max*temp/(1+temp);
return Kr;}

voidcorr_mix(){
float T[N],T_cel[N],K_c[N],K_r[N],corr_c[N],corr_r[N],plotdata[N],temp,gamma_s, m_mix, tt[N];
float x[N1],f[N1];

```

```

while(1){
    cout << "user menu:" << endl;
    cout << "0----specific heat correction vs Temperature" << endl;
    cout << "1----relaxation correction vs Temperature at 50kHz" << endl;
    cout << "2----corrections (including specific heat and relaxation) vs Temperature at 50kHz" << endl;
    cout << "3----relaxation correction vs Temperature of CO2:Ar=20:80 mixtures" << endl;
    cout << "4----transit time vs Temperature of different mixtures at 50kHz" << endl;
    cout << "q---quit" << endl;
    char choice;
    cin >> choice;

    if(!(choice=='q')){
        for(int p=0; p<N1;p++){

            if(choice=='0' || choice=='1' || choice=='2' || '4'){
                x[p]=0+0.1*p;
                f[p]=2*3.14*5*pow(10,4); }
            if(choice=='3') { x[p]=0.2;
                f[p]=2*3.14*pow(10,p);}
            m_mix=m_co2*x[p]+(1-x[p])*m_ar;
            gamma_s=(x[p]*7+(1-x[p])*5)/(x[p]*5+(1-x[p])*3);

            for(int i=0; i<N;i++){

                T[i]=T_min+step*i;
                T_cel[i]=T[i]-273.15;
                K_c[i]=K_sp(T[i],x[p]);
                K_r[i]=K_re(T[i],f[p],x[p]);
                corr_c[i]=K_c[i]+1;
                corr_r[i]=K_r[i]+1;
                temp=L*L*m_mix/(R*gamma_s*corr_c[i]*corr_r[i]*T[i]);
                tt[i]=pow(temp,0.5)*1e6;
                if(choice=='0') plotdata[i]=K_c[i];
                if(choice=='1' || '3') plotdata[i]=K_r[i];
                if(choice=='2') plotdata[i]=corr_c[i]*corr_r[i];
                if(choice=='4') plotdata[i]=tt[i];}

            if(p==0){ TGraph *gr0= new TGraph(N,T_cel, plotdata);
                gr0->SetLineColor(2); TMultiGraph *mg = new TMultiGraph();
                mg->Add(gr0); }
            if(p==1){ TGraph *gr1= new TGraph(N,T_cel, plotdata); mg->Add(gr1);}
            if(p==2) { TGraph *gr2= new TGraph(N,T_cel, plotdata); gr2->SetLineColor(3); mg->Add(gr2);}
            if(p==3){ TGraph *gr3= new TGraph(N,T_cel, plotdata); gr3->SetLineColor(4); mg->Add(gr3);}
            if(p==4){ TGraph *gr4= new TGraph(N,T_cel, plotdata); gr4->SetLineColor(5); mg->Add(gr4);}
            if(p==5){ TGraph *gr5= new TGraph(N,T_cel, plotdata); gr5->SetLineColor(6); mg->Add(gr5);}

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if(p==6){ TGraph *gr6= new TGraph(N,T_cel, plotdata); gr6->SetLineColor(7); mg->Add(gr6);}
if(p==7){ TGraph *gr7= new TGraph(N,T_cel, plotdata); gr7->SetLineColor(8); mg->Add(gr7);}
if(p==8){ TGraph *gr8= new TGraph(N,T_cel, plotdata); gr8->SetLineColor(9); mg->Add(gr8);}
if(p==9){ TGraph *gr9= new TGraph(N,T_cel, plotdata); gr9->SetLineColor(16); mg->Add(gr9);}
if(p==10){ TGraph *gr10= new TGraph(N,T_cel, plotdata); gr10->SetLineColor(26);
mg->Add(gr10);} }

if(choice=='0') mg->SetTitle("theoretical specific heat correction of CO2-Ar mixtures");
if(choice=='1') mg->SetTitle("theoretical relaxation correction of CO2-Ar mixtures at 50kHz, 1 atm");
if(choice=='2') mg->SetTitle("theoretical corrections (specific heat & relaxation) at 50kHz,1 atm, vs
Temperature of different mixtures");
if(choice=='3') mg->SetTitle("theoretical relaxation correction of 20:80 CO2_Ar mixture");
if(choice=='4') mg->SetTitle("transit time (including specific heat & relaxation corrections) at 1atm,
50 kHz, vs Temperature of different mixtures");
TCanvas* c1=new TCanvas("c1","",1);
c1->cd(1); mg->Draw("AC");
TLegend* l=new TLegend(0.8,0.6,0.9,0.90);
if(choice=='0'||choice=='1'||choice=='2'||choice=='4'){
    l->AddEntry(gr0,"pure Ar","L");
    l->AddEntry(gr1,"10% CO2","L");
    l->AddEntry(gr2,"20% CO2","L");
    l->AddEntry(gr3,"30% CO2","L");
    l->AddEntry(gr4,"40% CO2","L");
    l->AddEntry(gr5,"50% CO2","L");
    l->AddEntry(gr6,"60% CO2","L");
    l->AddEntry(gr7,"70% CO2","L");
    l->AddEntry(gr8,"80% CO2","L");
    l->AddEntry(gr9,"90% CO2","L");
    l->AddEntry(gr10,"100% CO2","L")}
if(choice=='3'){
    l->AddEntry(gr0,"f=1Hz","L");
    l->AddEntry(gr1,"f=10Hz","L");
    l->AddEntry(gr2,"f=100Hz","L");
    l->AddEntry(gr3,"f=1kHz","L");
    l->AddEntry(gr4,"f=10kHz","L");
    l->AddEntry(gr5,"f=100kHz","L");
    l->AddEntry(gr6,"f=1MHz","L");
    l->AddEntry(gr7,"f=10MHz","L");
    l->AddEntry(gr8,"f=100MHz","L");
    l->AddEntry(gr9,"f=1GHz","L");
    l->AddEntry(gr10,"f=10GHz","L");}
l->Draw();
c1->Update();}

if(choice=='q') return; } }

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