

Fundamental equation of state correlation with hybrid data sets

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A strategy is proposed for empirical fundamental equation of state correlations for pure fluids on the basis of hybrid data sets, composed of experimental and molecular simulation data. Argon and hydrogen chloride are used as examples.

Keywords: equation of state, molecular simulation, argon, hydrogen chloride

I. INTRODUCTION

The fundamental equation of state (FEOS) can be expressed with various thermodynamic potentials¹, e.g. internal energy $E(N, V, S)$, enthalpy $H(N, p, S)$, Helmholtz energy $F(N, V, T)$ or Gibbs energy $G(N, p, T)$, with number of particles N , volume V , pressure p , temperature T and entropy S . Any other thermodynamic property, which may or may not be measurable in the laboratory, is a linear or non-linear combination of derivatives with respect to the independent variables. Conceptual details for the present context are outlined in references^{2,3}. The form $F/T(N, V, 1/T)$ is preferred for empirical correlations due to practical reasons⁴. A definition for its derivatives may be

$$\frac{\partial^{m+n}(F/(RT))}{\partial \beta^m \partial \rho^n} \beta^m \rho^n \equiv A_{mn} = A_{mn}^i + A_{mn}^r, \quad (1)$$

where R is the gas constant, $\beta \equiv 1/T$ and $\rho \equiv N/V$. A_{mn} can be separated into an ideal part A_{mn}^i and a residual part A_{mn}^r ⁵. The ideal part can usually be obtained by independent means, e.g. spectroscopic data or ab initio calculation^{3,6,7}. It is the residual part which is of concern here.

An empirical FEOS correlation needs carefully selected thermodynamic data to be used in a fitting procedure. Unfortunately, the data availability today is insufficient. FEOS correlations with technical accuracy⁴ covering the entire fluid region of technological interest are available for about 100 of roughly 1000 pure compounds of industrial relevance. For the remaining compounds, data sets are at best scarce so that FEOS correlations are hardly feasible. For mixtures, of course, the data availability is much worse.

It is to be expected that the accuracy of the Helmholtz energy surface representation will increase if more A_{mn} are used in fitting eq. (1). Consequently, the accuracy of any other thermodynamic property obtained from the

FEOS should also increase. However, the overall information on the whole possible range of Helmholtz energy derivatives from laboratory measurements is limited: $A_{01}^r = p/(\rho RT) - 1$, $A_{10}^i + A_{10}^r = H/(RT) - A_{01}^r - 1$ and $A_{20}^i + A_{20}^r = -C_v/R$, where C_v is the isochoric heat capacity. A_{11} and A_{02} cannot be accessed individually, because the measurable quantities, isobaric heat capacity C_p and speed of sound w , are non-linear combinations of A_{01} , A_{20} , A_{11} and A_{02} . In molecular simulation such constraints can be entirely removed. The statistical mechanical formalism proposed by Lustig allows for the simultaneous sampling of any A_{mn}^r in a single NVT simulation for a given state point^{2,3}.

II. MOLECULAR SIMULATION AND FEOS CORRELATION

Recent progress in molecular simulation has shown that molecular interaction models have powerful predictive capabilities with respect to thermodynamic data⁸. The current standard is to match molecular models to real compounds based on laboratory vapor-liquid equilibrium (VLE) data. The typical accuracy of reproduction is $\pm 5\%$ for vapor pressure and $\pm 1\%$ for saturated liquid density⁹⁻¹⁶. However, it is usually not known how molecular interaction models perform in homogeneous regions. We performed simulations for some ten molecular models⁹⁻¹⁶ representing fluids of very different nature at various state points in the homogeneous regions, and compared A_{mn}^r results with the best available FEOS correlations from the literature. The results for hydrogen sulfide are shown in figure 1 as an example. There is agreement with the FEOS of Lemmon and Span¹⁷ throughout. Only A_{02}^r shows a deterioration, which was not considered individually in the fits of the FEOS¹⁷. Tests for other fluids also show promising behavior. Additional examples (including argon and hydrogen chloride) are given in the supplementary material. We conclude that molecular interaction models may perform well in the fluid region, based on comparisons to reference FEOS correlations.

Therefore, a valid FEOS correlation can be established

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based on laboratory VLE data and molecular simulation data covering the homogeneous fluid regions. This approach targets fluids for which no laboratory data in the homogeneous fluid regions are available. With such hybrid data employment, the construction of an FEOS amounts to investments of days rather than years common for the exclusively experimental route. Using VLE data from laboratory experiments rather than obtaining them from molecular simulation is still advised. Typical uncertainties (see above) of directly simulated VLE data are usually too high for technical quality FEOS development. In this paper, two examples are presented: argon and hydrogen chloride.

The underlying experimental VLE data sets as well as the ideal part of the Helmholtz energy in eq. (1) were adopted from the FEOS correlations^{18,19}. Extensive data sets in the homogeneous fluid regions were generated using the molecular simulation tool *ms2*²⁰ that currently supports the derivatives A_{00}^r , A_{10}^r , A_{01}^r , A_{20}^r , A_{11}^r , A_{02}^r , A_{30}^r , A_{21}^r and A_{12}^r . The simulations used molecular interaction models fitted to experimental VLE data of argon and hydrogen chloride^{9,16}. The resulting data sets cover large portions of the homogeneous fluid regions: 155 state points for argon and 61 for hydrogen chloride with nine A_{mn}^r at each state point. Throughout, 256 particles were sufficiently equilibrated and then run for 2 million production cycles with *NVT* Monte Carlo simulations²¹. Electrostatic long-range corrections were approximated by the reaction field method²². The residual Helmholtz energy was determined by Widom's test particle insertion²³. Results were validated with simulations of $N=800$ and 1372 particles. System size effects were found generally insignificant for the current purpose.

The employed correlations are explicit in terms of the residual Helmholtz energy as is common in modern FEOS development⁴

$$A_{00}^r = \sum_{k=1}^{I_P} n_k \tau^{t_k} \delta^{d_k} + \sum_{k=I_P+1}^{I_P+I_E} n_k \tau^{t_k} \delta^{d_k} \exp(-\delta^{l_k}) + \sum_{k=I_P+I_E+1}^{I_P+I_E+I_G} n_k \tau^{t_k} \delta^{d_k} \exp(-\eta_k(\delta - \epsilon_k)^2 - \lambda_k(\tau - \gamma_k)^2), \quad (2)$$

with I_P polynomial, I_E exponential and I_G Gaussian bell-shaped terms. $\delta = \rho/\rho_c$ and $\tau = T_c/T$, where ρ_c and T_c are the critical density and critical temperature, respectively. Sole fitting of coefficients n_k is straightforward²⁴. However, the core of FEOS correlation is the simultaneous optimization of I_P , I_E , I_G , t_k , d_k , l_k , η_k , ϵ_k , λ_k , γ_k , which requires the expert use of complex nonlinear fit algorithms^{4,25}. Fitting procedures employed in this work follow the outlines of Lemmon and Jacobsen²⁵. The numerical values for the parameters of the present FEOS correlations are given in the supplementary material. Here, we report on preliminary progress over standard procedures utilizing molecular simulation data. The

presented results are from preliminary FEOS optimizations of eq. (2). Improvements are in progress and will be reported (in all detail) in due course.

The most accurate FEOS^{18,19} available in the literature reproduce experimental vapor pressures p_v within $\pm 0.02\%$ and saturated liquid densities ρ' within $\pm 0.01\%$ for argon and $\pm 1.0\%$ (p_v) and $\pm 1.5\%$ (ρ') for hydrogen chloride. Deviations tend to be higher near the critical point. The present FEOS are nearly as accurate: p_v is reproduced within $\pm 0.03\%$ and ρ' within $\pm 0.1\%$ for argon. For hydrogen chloride the results from the experimentally designed FEOS and the present FEOS are about identical. VLE deviation plots are given in the supplementary material.

In figure 2, the present FEOS is compared with the reference FEOS for argon. For both FEOS, the basis of the comparison is the same set of laboratory data gathered from the homogeneous fluid regions. Here, only the most trustworthy laboratory data are considered. Note that for the present FEOS no laboratory data in the homogeneous regions were used for the fits. Argon is a well studied fluid and the FEOS of Tegeler et al.¹⁸ can be viewed as complete thermodynamic knowledge. In comparison, the new approach proves to be quite effective.

Figure 3 shows hydrogen chloride. No useful experimental data for C_v , C_p or w are available in the homogeneous regions, leaving density only for comparison. The present and the reference FEOS exhibit similar performance. The present FEOS, however, was constructed with a much larger set of independent A_{mn}^r . It is therefore reasonable to assume superior predictions for the remaining thermodynamic properties. In such cases, when experimental data are not available, molecular simulation can be used to enlarge data sets or to increase the range of validity of FEOS correlations to state points difficult to access in the laboratory.

III. CONCLUSIONS

A strategy is proposed for empirical FEOS correlations based on laboratory VLE data and molecular simulation data at homogeneous fluid states. For many substances sufficient VLE data are available. However, experimental data at homogeneous states are usually scarce or unavailable. Molecular simulation can provide such data with little time and cost effort. Sufficient accuracy for truly independent thermodynamic properties is feasible for practical application in process design and technical quality FEOS correlation. Extensions to a variety of pure compounds and their mixtures are in progress.

SUPPLEMENTARY MATERIAL

Supplementary material associated with this article can be found at [URL inserted by AIP]

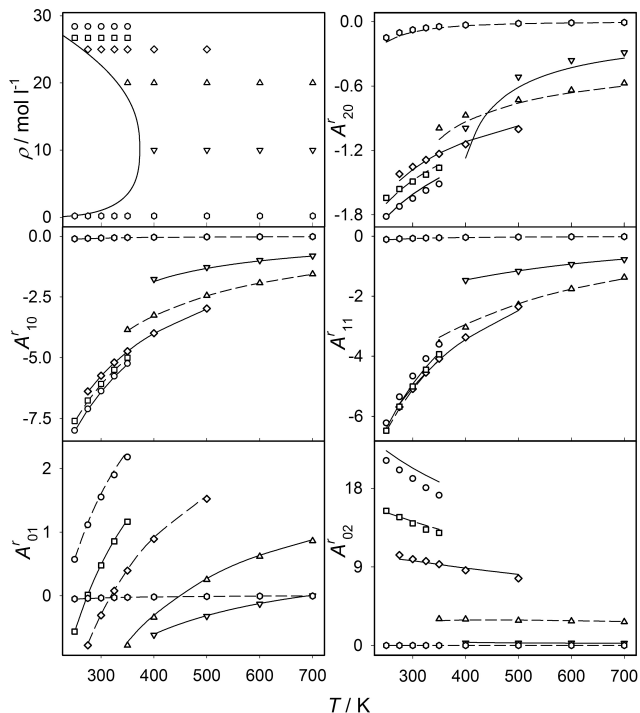


FIG. 1. Distribution of simulated state points for hydrogen sulfide¹³ in the temperature–density plane (top left). Corresponding A_{mn}^r at the same state points (remaining subfigures), excluding the two phase region. Different symbols denote isochores. Lines correspond to the FEOS of Lemmon and Span¹⁷. Statistical uncertainties of the simulation data do not exceed symbol sizes.

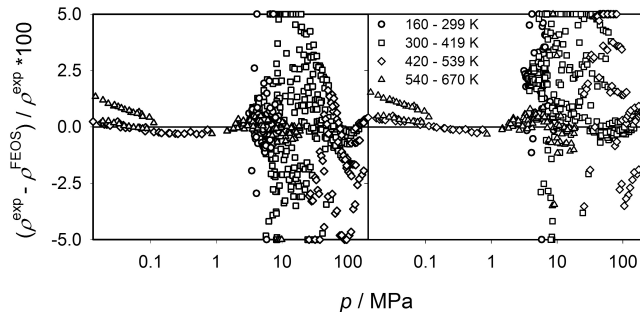


FIG. 3. Relative deviations of laboratory density data (symbols) from values of the FEOS of Thol¹⁹ (left) and the present FEOS (right) for hydrogen chloride. Details are in the supplementary material. Symbols exceeding the axis limits were placed on the borders.

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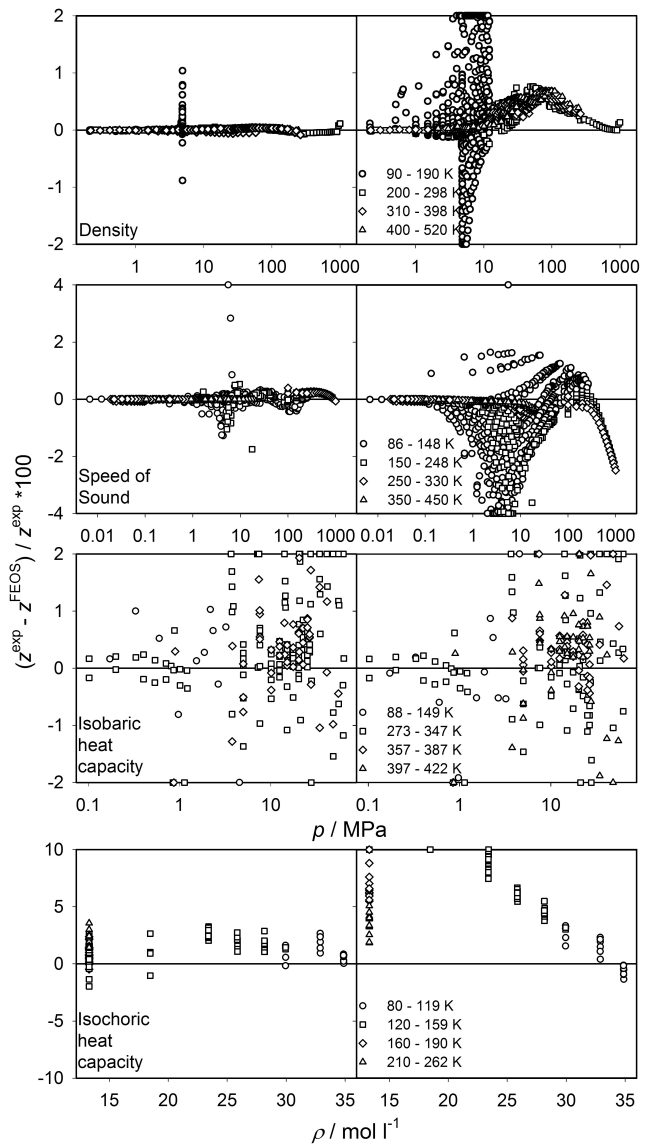


FIG. 2. Relative deviations of experimental density, isochoric and isobaric heat capacity and speed of sound data (symbols) from values of the FEOS of Tegeler et al.¹⁸ (left) and the present FEOS (right) for argon. Details are in the supplementary material. Symbols exceeding the axis limits were placed on the borders.

were performed on the Cray XE6 (Hermit) at the High Performance Computing Center Stuttgart (HLRS). The authors wish to thank Andreas Köster for setting up and running simulations and helping to prepare the figures. Additionally, we would like to thank Sebastian Hielscher for his help during the development of the equations of state.

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Supporting Information to: Fundamental equation of state correlation with hybrid data sets

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This supplementary material contains the parameters of the FEOS correlation developed in this work. These FEOS correlations are also attached as *.fld files that may serve as input files for the software REFPROP¹ distributed by NIST. Note that the present FEOS correlations are not intended to supersede the existing ones, they are rather a proof of concept for the hybrid fitting approach. Detailed information for the laboratory data shown in the deviation plots of the corresponding article, as well as additional figures comparing Helmholtz energy derivatives from molecular simulation with the best available FEOS correlations available in literature are also presented.

FEOS CORRELATION

The ideal part of A_{00} was taken from literature^{2,3}:

$$A_{00}^i = \ln(\delta) + 1.5\ln(\tau) + a_1 + a_2\tau$$

for argon and

$$A_{00}^i = \ln(\delta) + b_0\ln(\tau) + b_1/\tau + b_2/\tau^2 + b_3\ln(1 - \exp(-b_4\tau)) + a_1 + a_2\tau$$

for hydrogen chloride, where $\delta = \rho/\rho_c$, $\tau = T_c/T$, ρ_c and T_c are the critical density and critical temperature, respectively. The residual part of A_{00} is given by

$$A_{00}^r = \sum_{k=1}^{I_P} n_k \tau^{t_k} \delta^{d_k} + \sum_{k=I_P+1}^{I_P+I_E} n_k \tau^{t_k} \delta^{d_k} \exp(-\delta^{l_k}) + \sum_{k=I_P+I_E+1}^{I_P+I_E+I_G} n_k \tau^{t_k} \delta^{d_k} \exp(-\eta_k(\delta - \epsilon_k)^2 - \lambda_k(\tau - \gamma_k)^2),$$

T_c and ρ_c , the coefficients n_k , temperature t_k and density d_k exponents, as well as the remaining parameters a_k , b_k , l_k , η_k , λ_k , ϵ_k and γ_k are listed in table I, II, III and IV.

TABLE I. Parameters for A_{00}^i

Ar	HCl
$b_0 = 2.5000000000000E+00$	$a_1 = 8.31666243E+00$
$b_1 = -4.14993688013617E-03$	$a_2 = -4.94651164E+00$
$b_2 = 8.01920206324877E-05$	
$b_3 = 1.05439208014000E+00$	
$b_4 = 1.24113767762458E+01$	
$a_1 = 2.23691468323703E+01$	
$a_2 = -1.04426386530984E+03$	

TABLE II. Parameters for A_{00}^r (Ar)

k	n_k	t_k	d_k	l_k	η_k	λ_k	γ_k	ϵ_k
1	0.9203857634345E-02	1.0000	4					
2	0.4420259372220E+01	0.2417	1					
3	-0.3011388446818E+01	0.2350	1					
4	0.2383462099031E+01	1.0500	2					
5	-0.3793401117482E+01	1.0070	2					
6	0.2734934938763E+00	0.7980	3					
7	-0.1758778579302E+01	1.1130	1	1				
8	-0.1202948335629E+01	0.3530	1	2				
9	-0.7520097665167E+00	0.2680	3	2				
10	-0.3939012801387E+00	0.1000	2	1				
11	-0.5051199103071E-01	3.2000	2	2				
12	-0.2218746641729E-01	1.6300	4	1				
13	0.7822742439858E+00	0.1920	1		0.7820	0.8050	0.6790	0.7250
14	-0.3323060296311E+00	2.1700	1		1.5080	0.5440	0.3320	2.4160
15	-0.2556198451750E+00	0.3680	3		1.0600	0.7030	0.5700	0.8440
16	-0.2268076587044E-01	0.8700	5		1.2690	0.6890	1.1400	1.7750
17	-0.9044770262982E-01	0.8560	2		2.5290	1.8670	0.4250	0.8940
18	-0.2473301461958E+00	1.0100	1		2.2360	1.0870	0.3250	0.5170
19	0.2744619756963E-01	1.5600	2		13.8800	7.1320	1.7890	1.1140
20	0.1383935651711E+00	1.4260	3		1.3790	0.6300	0.8460	2.1190

TABLE III. Parameters for A_{00}^r (HCl)

k	n_k	t_k	d_k	l_k	η_k	λ_k	γ_k	ϵ_k
1	-1.074373604174E-03	1.000	4					
2	3.572465086841E+00	0.527	1					
3	-4.506626372912E+00	0.797	1					
4	-6.434414692419E-01	1.000	2					
5	3.889139266238E-01	0.825	3					
6	-7.670583344849E-01	3.282	1	2				
7	-5.769769651966E-01	3.790	3	2				
8	4.569711619378E-01	0.720	2	1				
9	7.768169923568E-02	4.620	2	2				
10	-3.096474456962E-02	0.836	7	1				
11	5.351691408157E-01	2.510	1		0.984	0.517	1.286	0.679
12	7.379127869527E-02	0.812	1		1.770	0.224	0.460	1.230
13	-5.858713493938E-02	2.610	3		1.700	0.420	0.567	0.857
14	-1.046501746496E+00	2.190	3		29.180	57.700	1.366	0.922

TABLE IV. Critical temperature and critical density

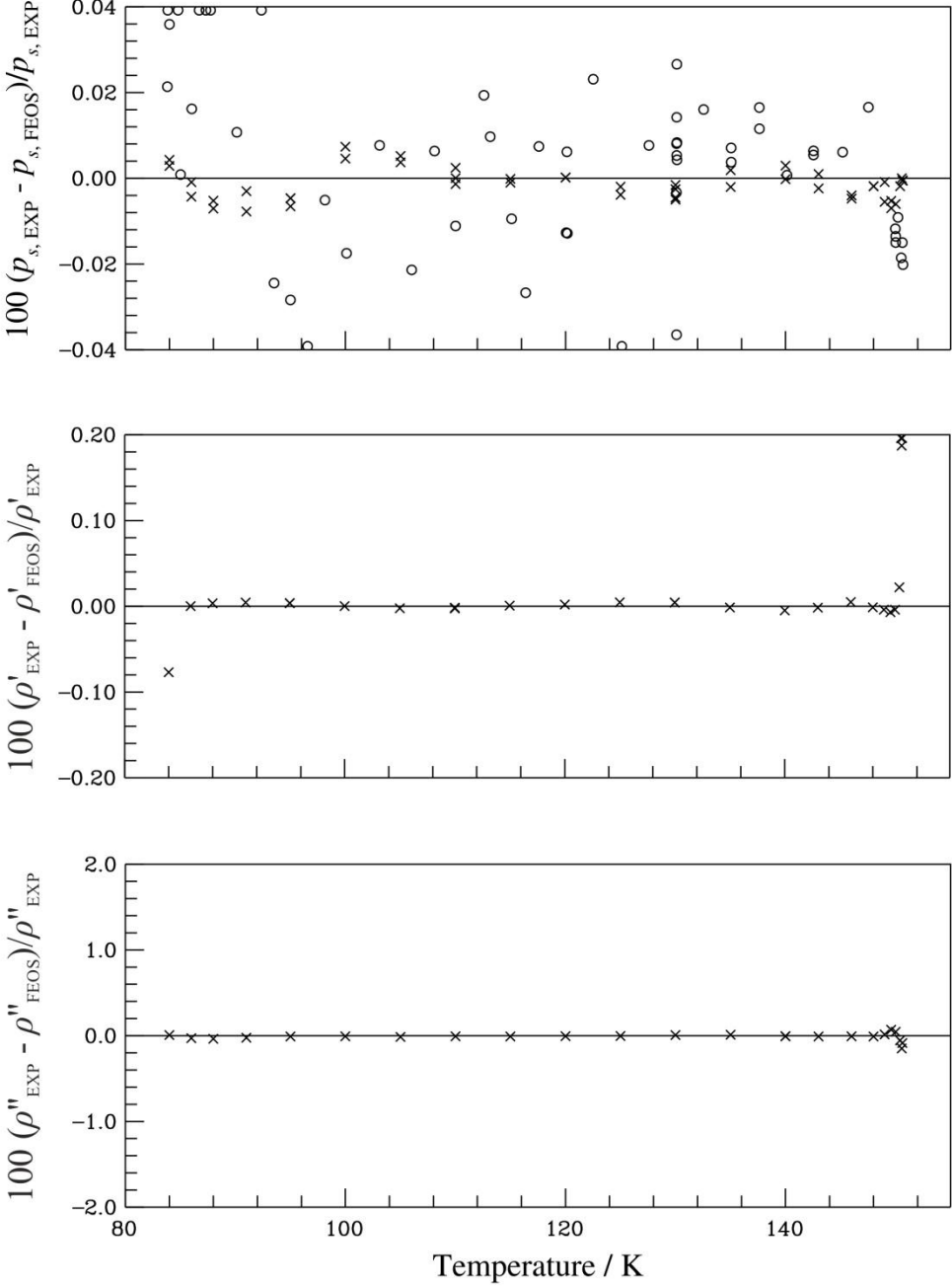
	T_c /K	ρ_c /(mol/l)
Ar	150.696	13.416
HCl	324.55	11.55

¹“Nist reference fluid thermodynamic and transport properties database,” <http://www.nist.gov/srd/nist23.cfm>.

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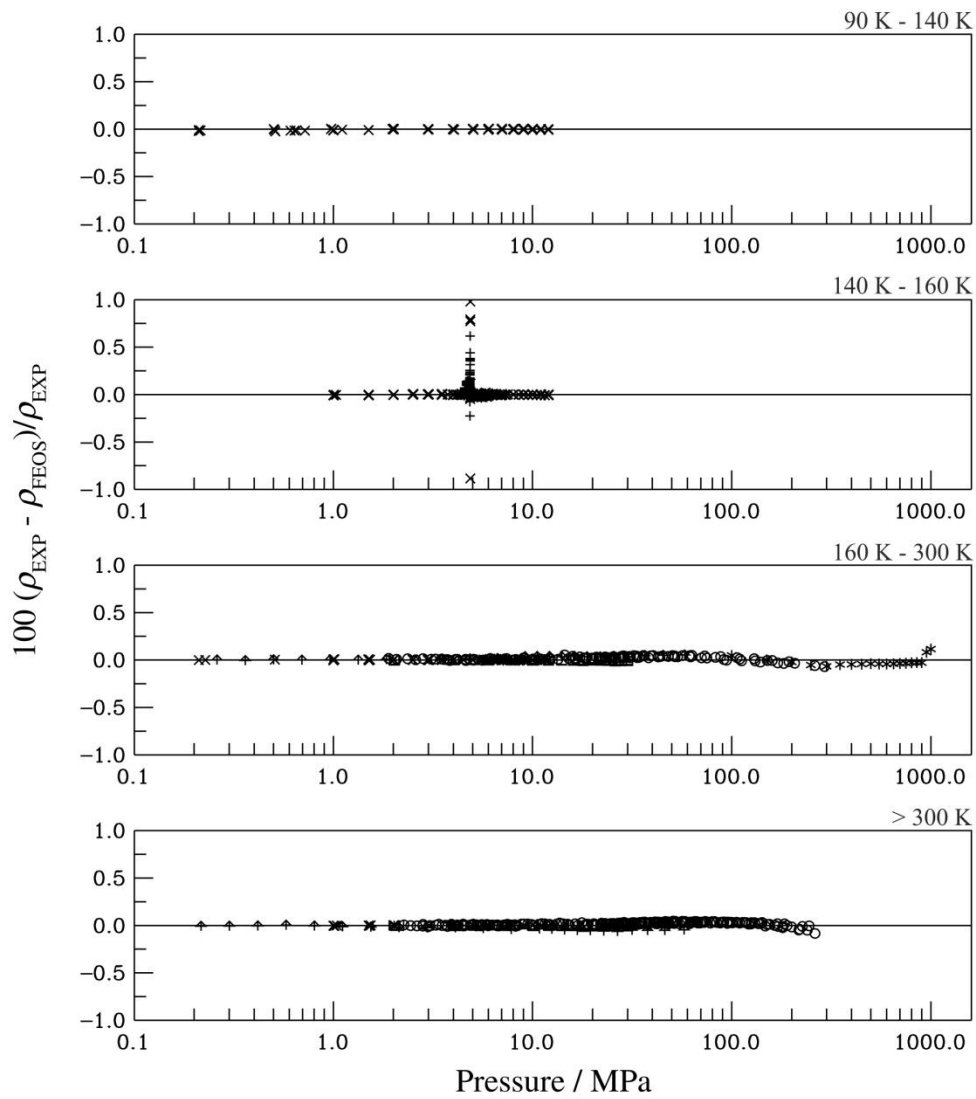
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Relative deviations of laboratory vapor pressure (p_s), saturated liquid density (ρ'), saturated vapor density (ρ''), density (ρ), isochoric heat capacity (C_v), isobaric heat capacity (C_p) and speed of sound (w) data from the **FEOS of Tegeler *et al.* (1999)** for **argon**



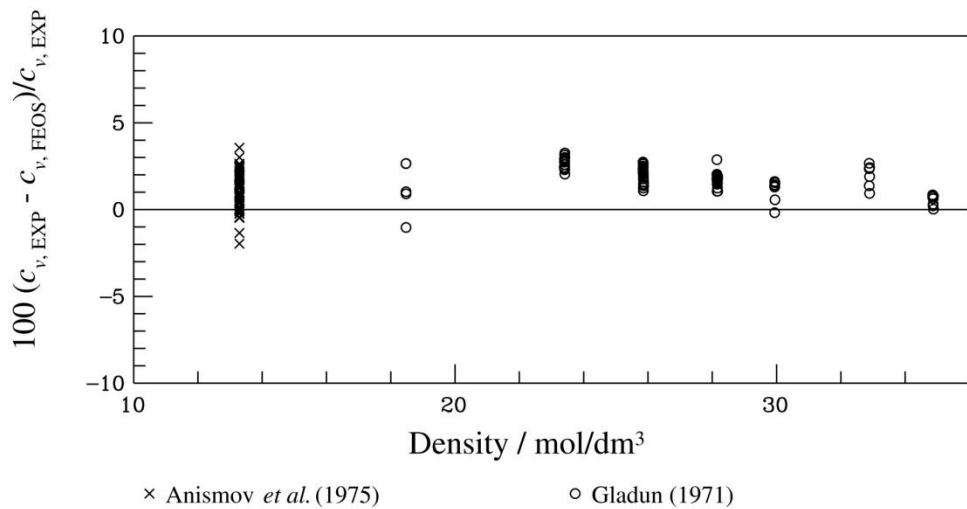
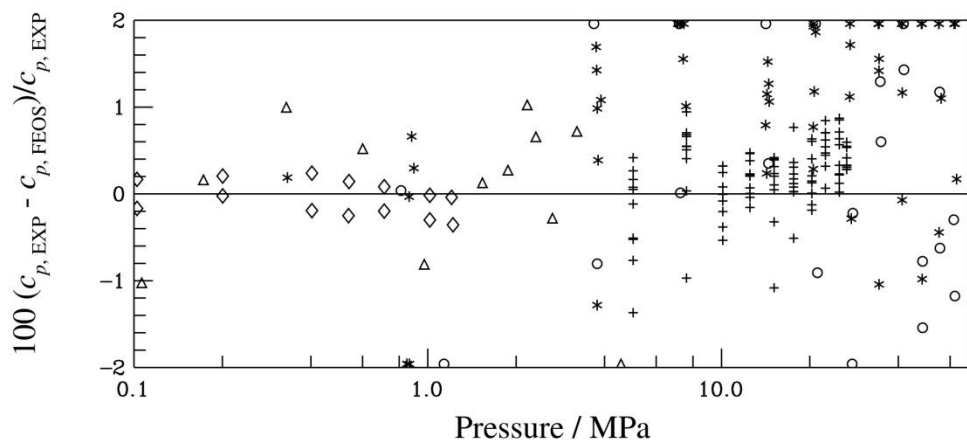
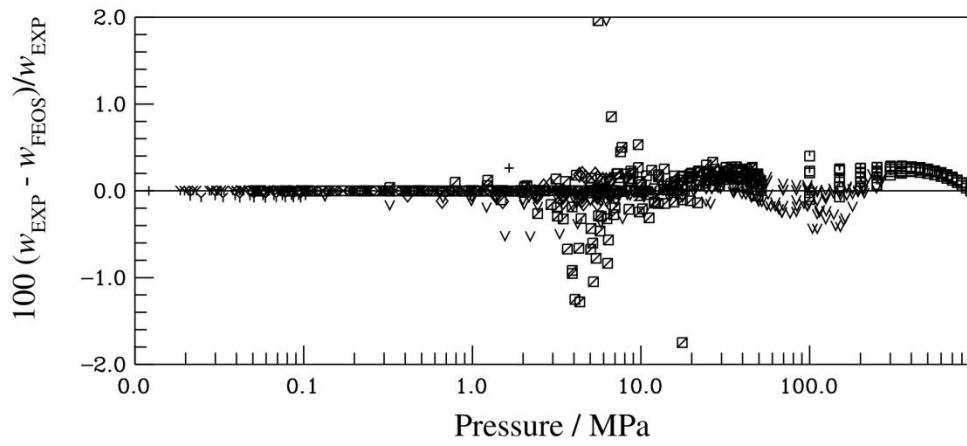
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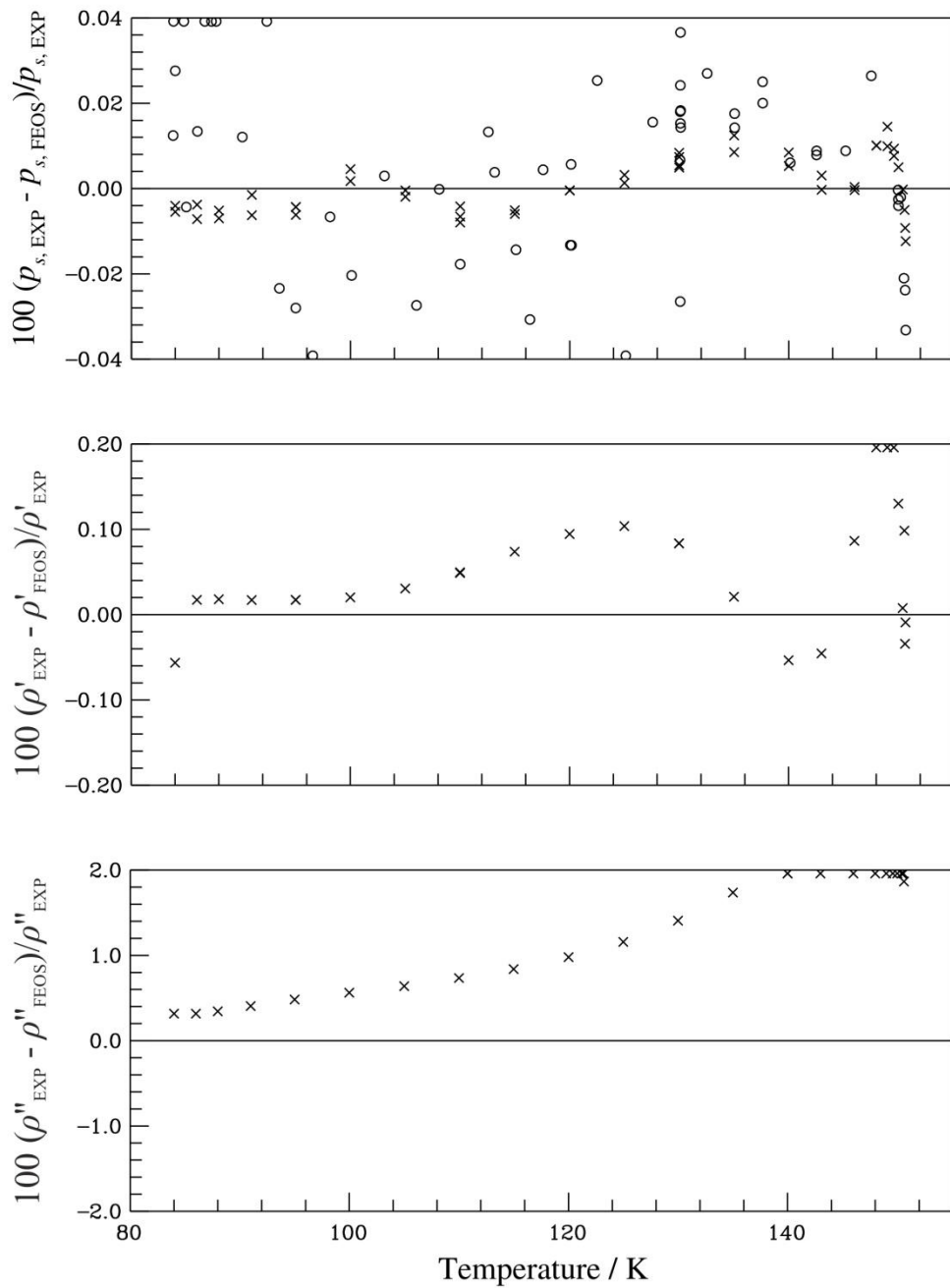


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 * Biswas *et al.* (1988)
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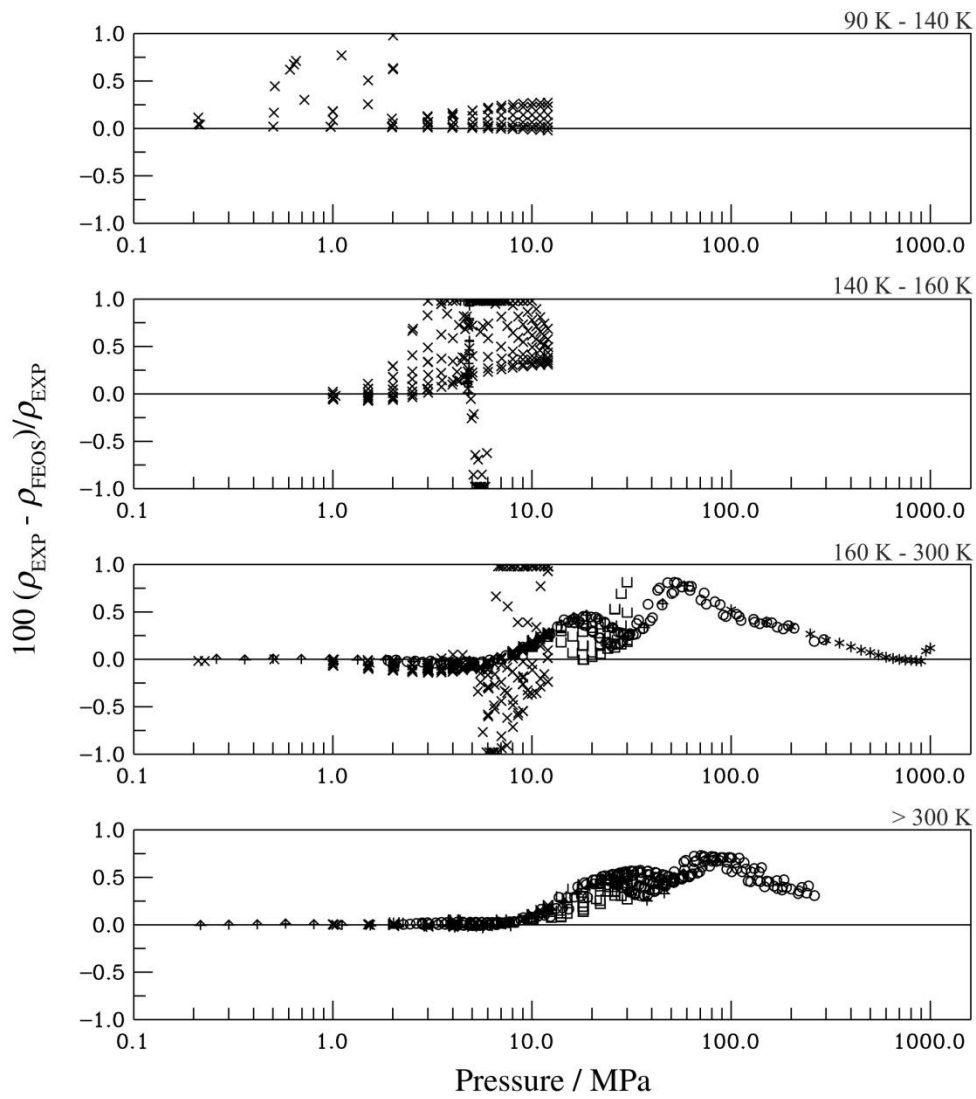


Relative deviations of laboratory vapor pressure (p_s), saturated liquid density (ρ'), saturated vapor density (ρ''), density (ρ), isochoric heat capacity (C_v), isobaric heat capacity (C_p) and speed of sound (w) data from the **present FEOS** for **argon**



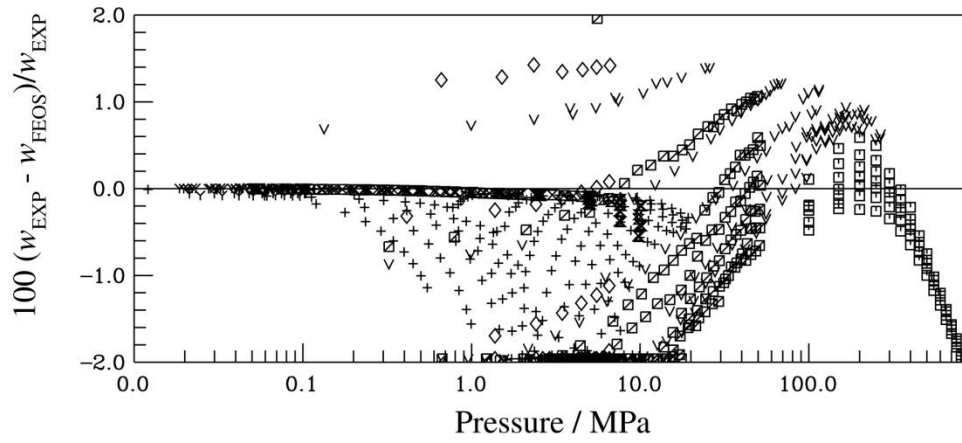
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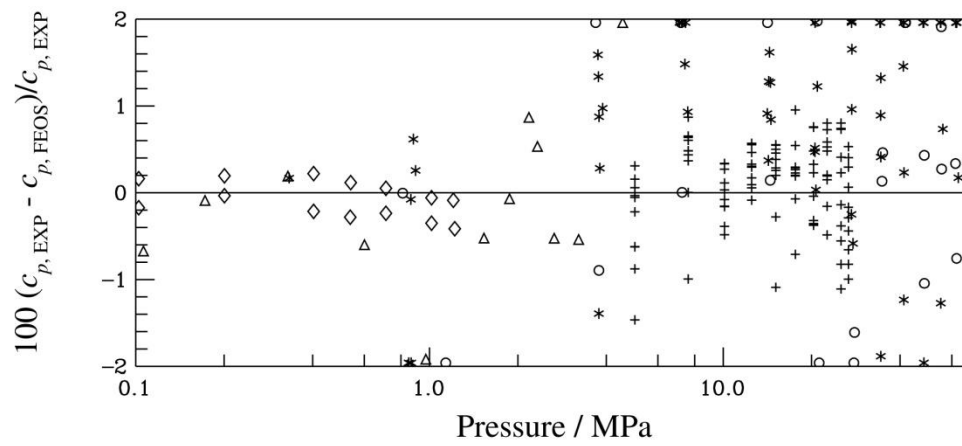


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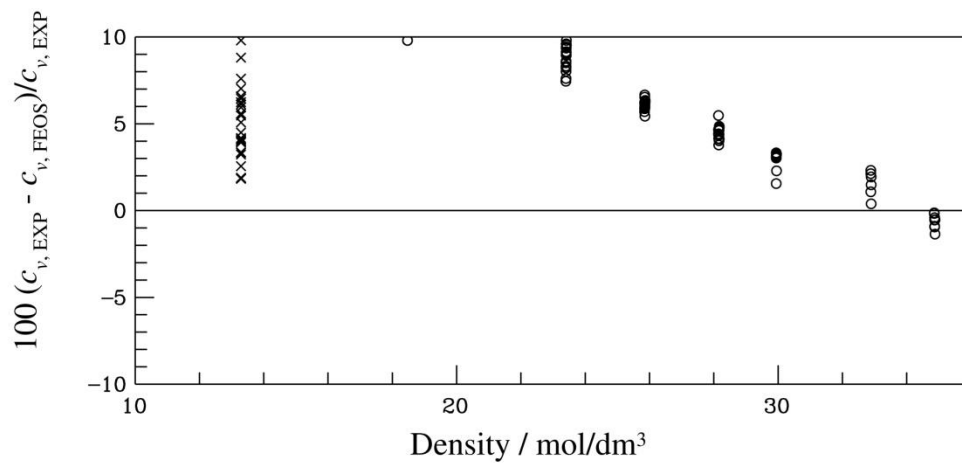
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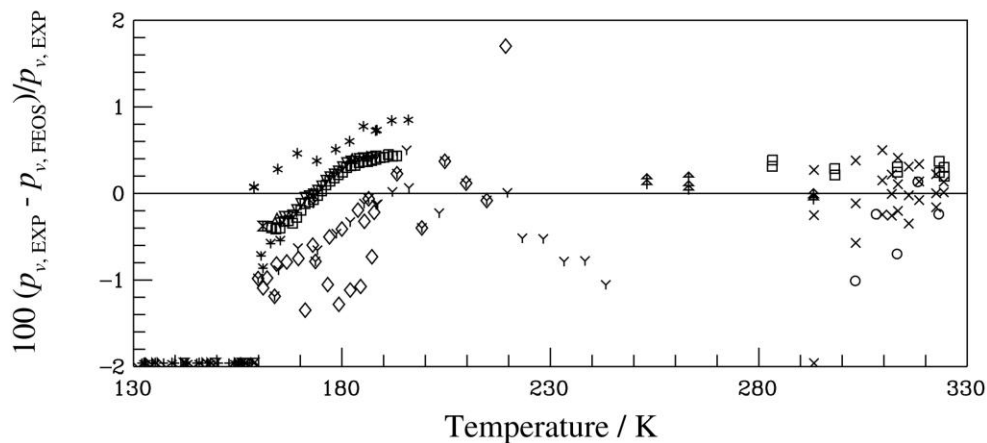
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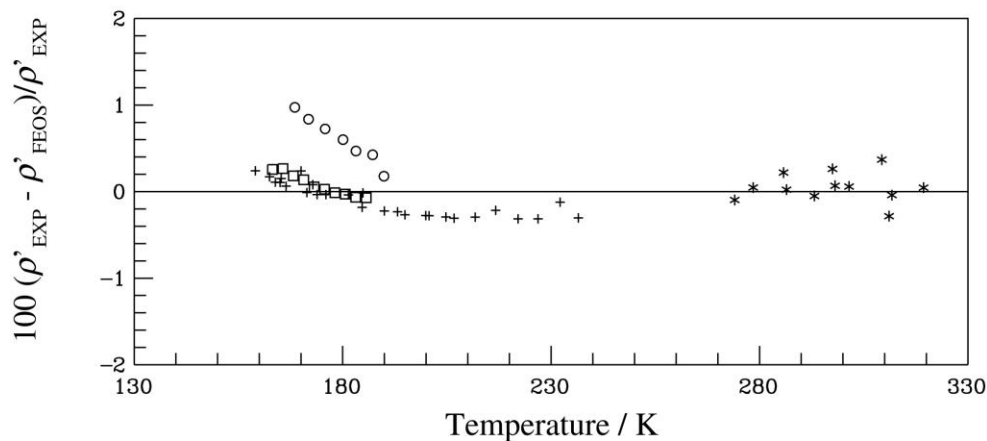
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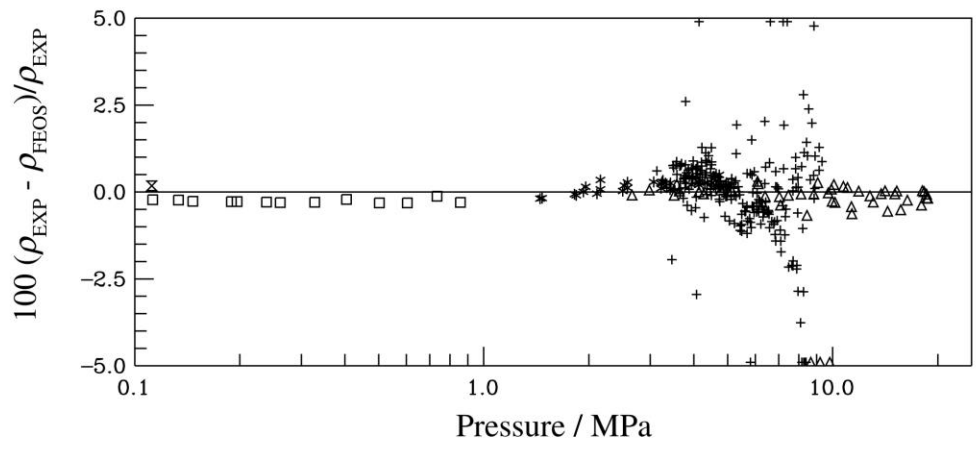
Relative deviations of laboratory vapor pressure (p_v), saturated liquid density (ρ') and density (ρ) data from the **FEOS of Thol(2010)** for **hydrogen chloride**



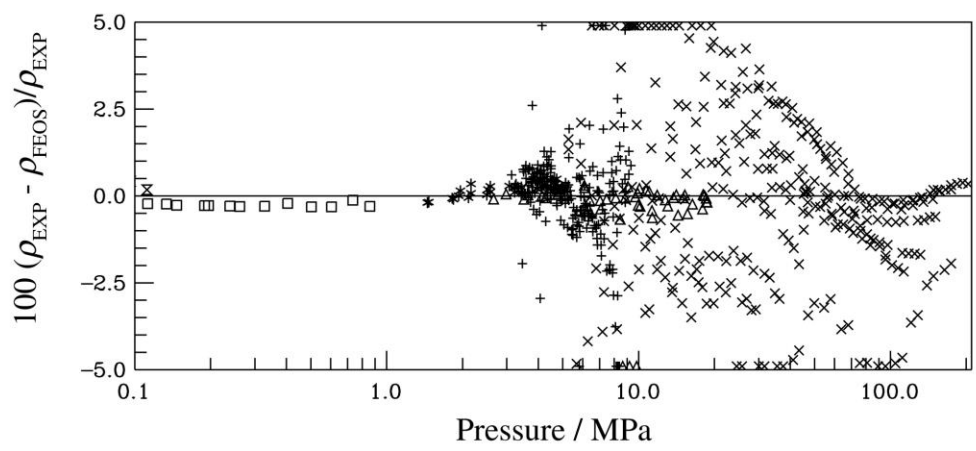
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|------------------------------|------------------------------------|
| + Chihara & Inaba (1976) | × Dorsman (1908) |
| □ Florisse & Peters (2002) | ○ Franck <i>et al.</i> (1962) |
| * Giauque & Wiebe (1928) | ◇ Henderson <i>et al.</i> (1986) |
| ⊗ Henglein (1923) | △ Henning & Stock (1921) |
| ▷ Karwat (1924) | ∇ Nunes da Ponte & Staveley (1981) |
| † Preuss & Moerke (1988) | □ Stock (1923) |
| ∇ Stock <i>et al.</i> (1921) | |



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|----------------------------------|----------------------------|
| + Henderson <i>et al.</i> (1986) | □ Shapiro & Sadoway (1996) |
| ○ Steele <i>et al.</i> (1906) | * Thomas (1962) |

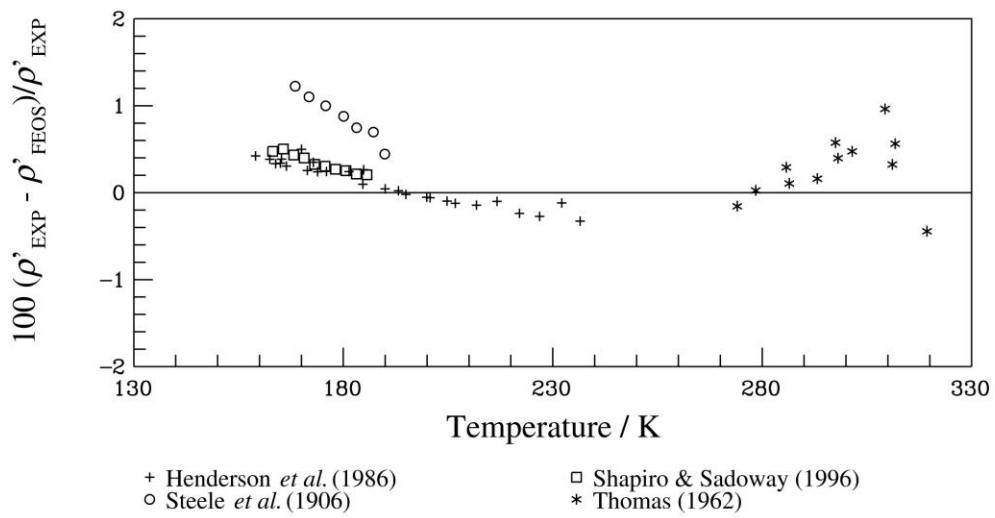
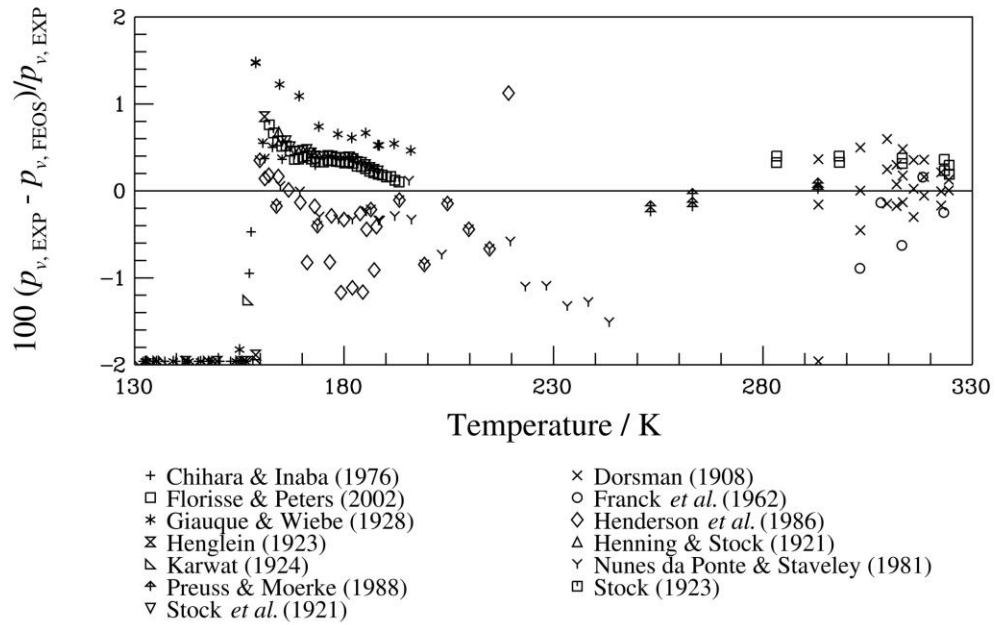


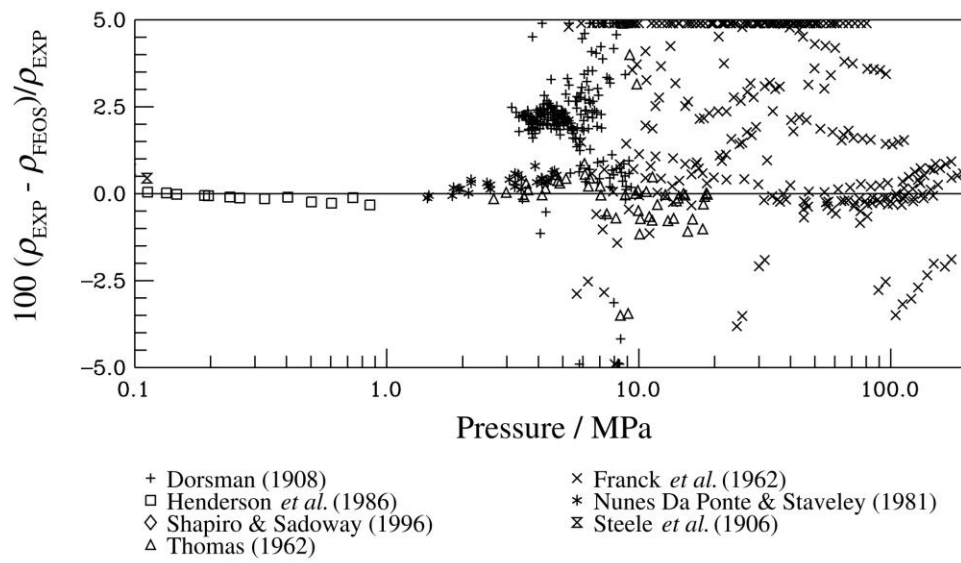
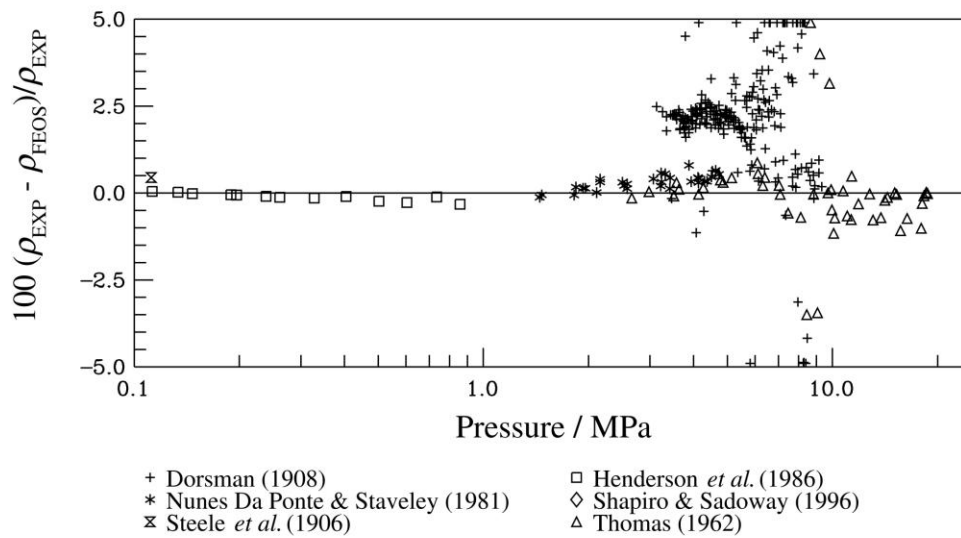
- + Dorsman (1908)
- * Nunes Da Ponte & Staveley (1981)
- ⊠ Steele *et al.* (1906)
- Henderson *et al.* (1986)
- ◇ Shapiro & Sadoway (1996)
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- + Dorsman (1908)
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- × Franck *et al.* (1962)
- * Nunes Da Ponte & Staveley (1981)
- ⊠ Steele *et al.* (1906)

Relative deviations of laboratory vapor pressure (p_v), saturated liquid density (ρ') and density (ρ) data from the **present FEOS** for **hydrogen chloride**





FEOS

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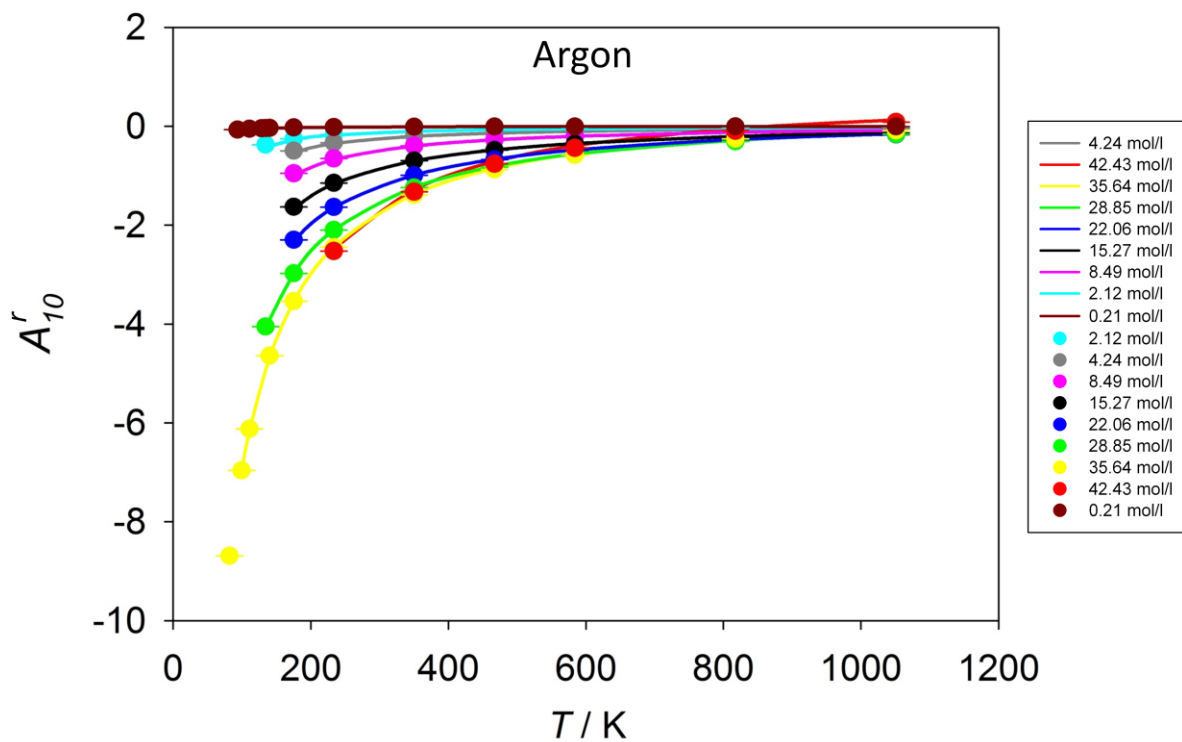
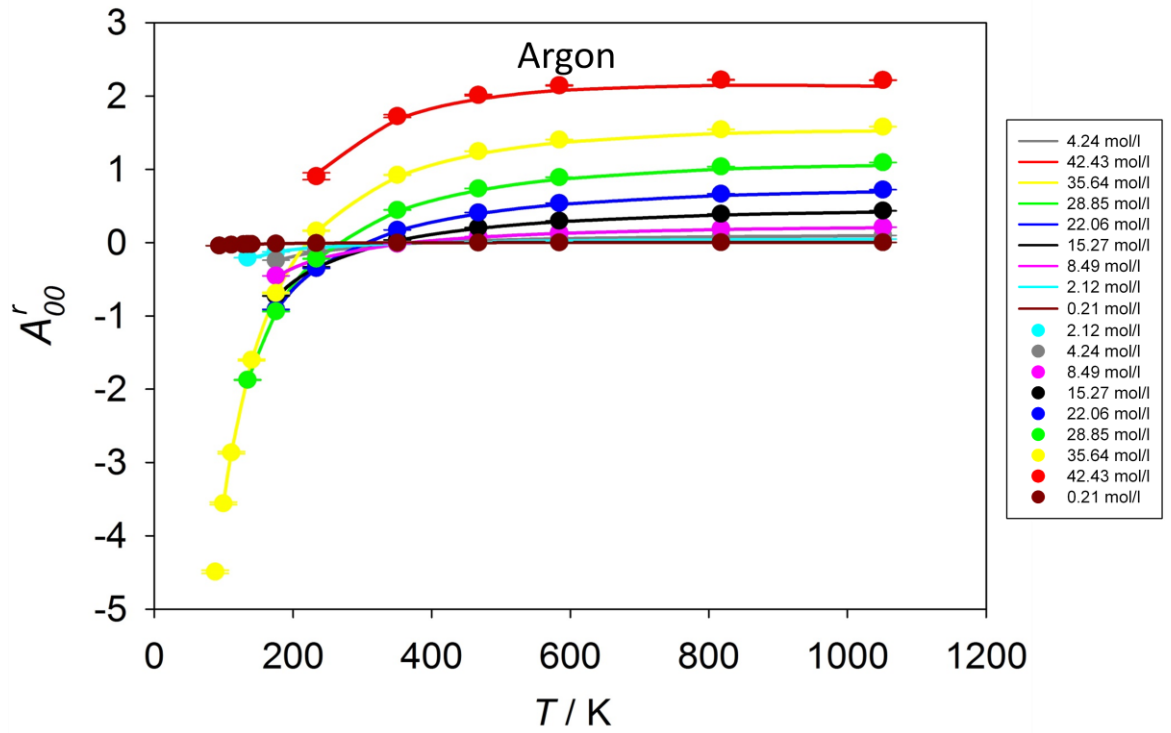
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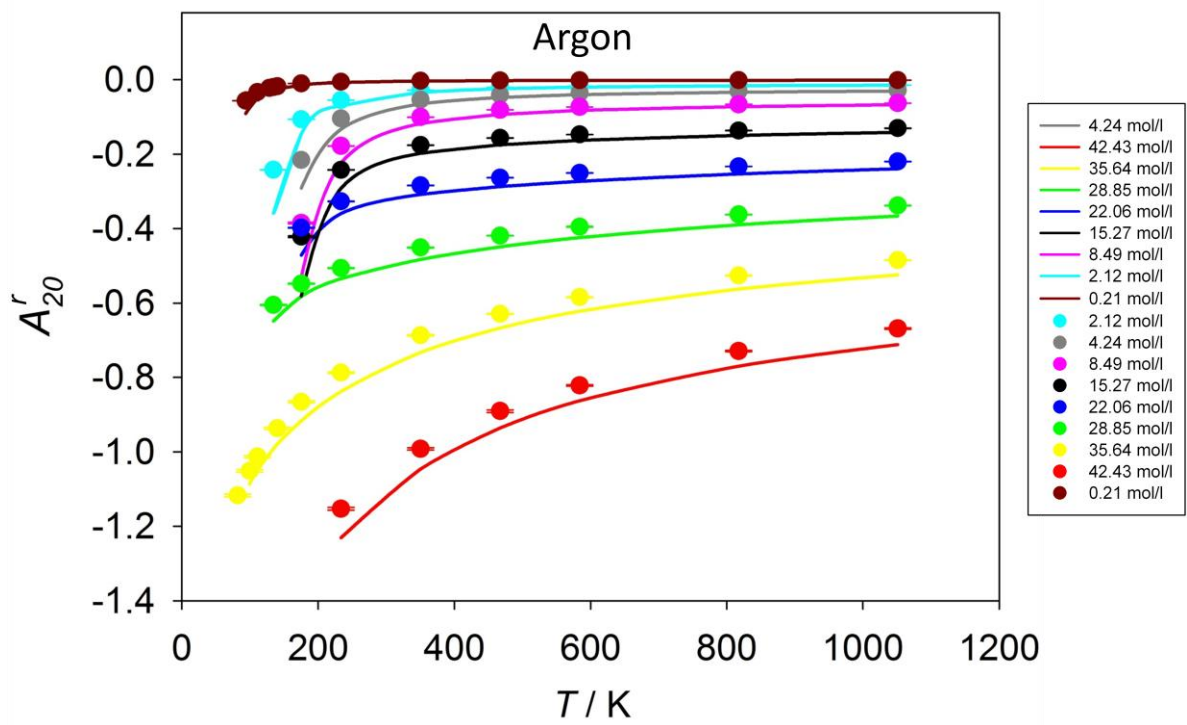
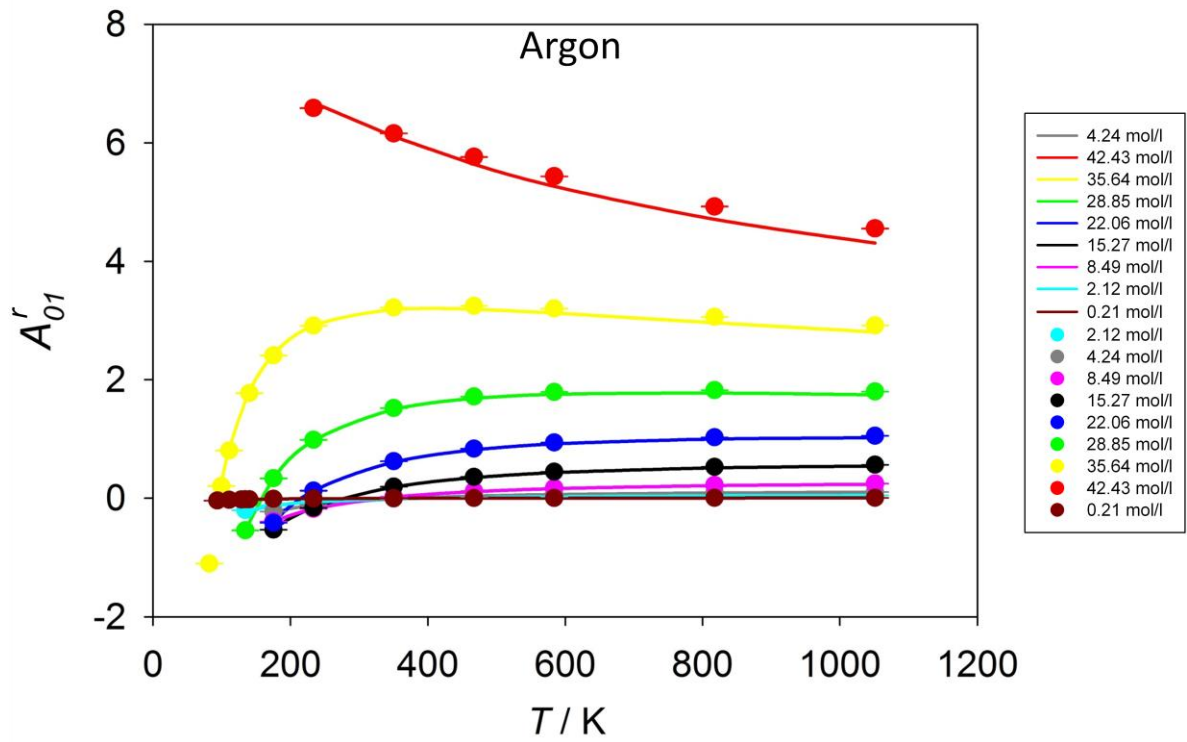
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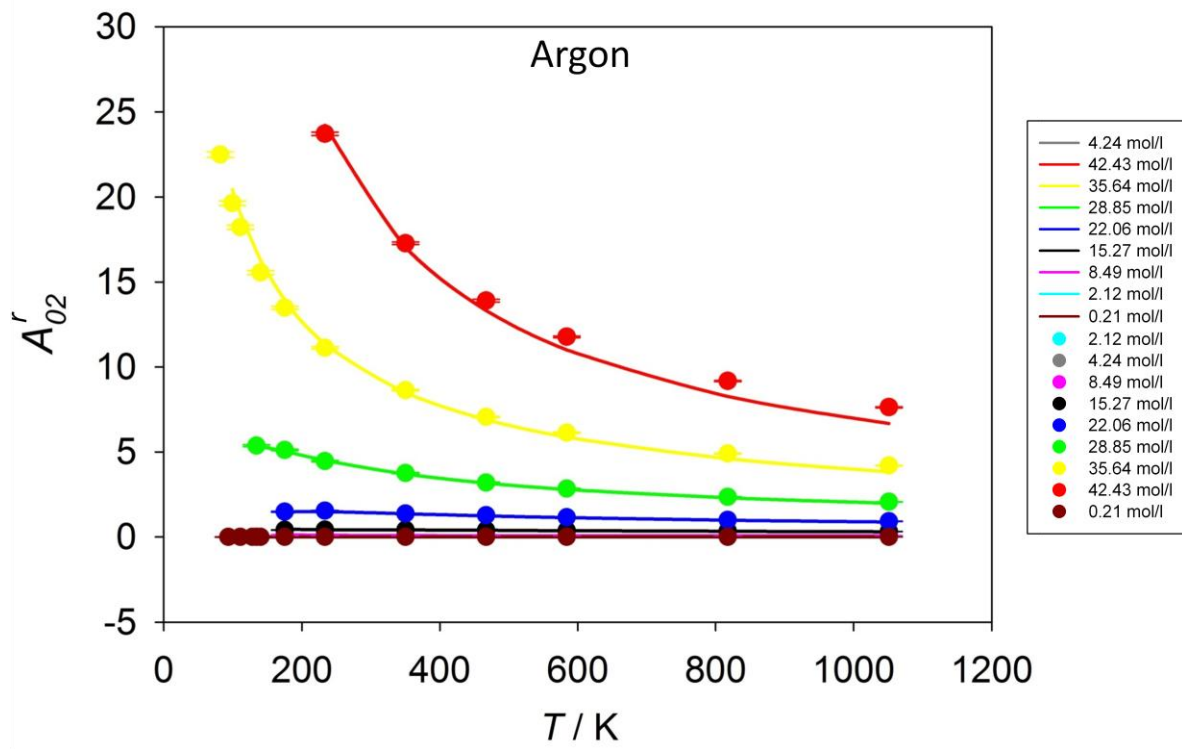
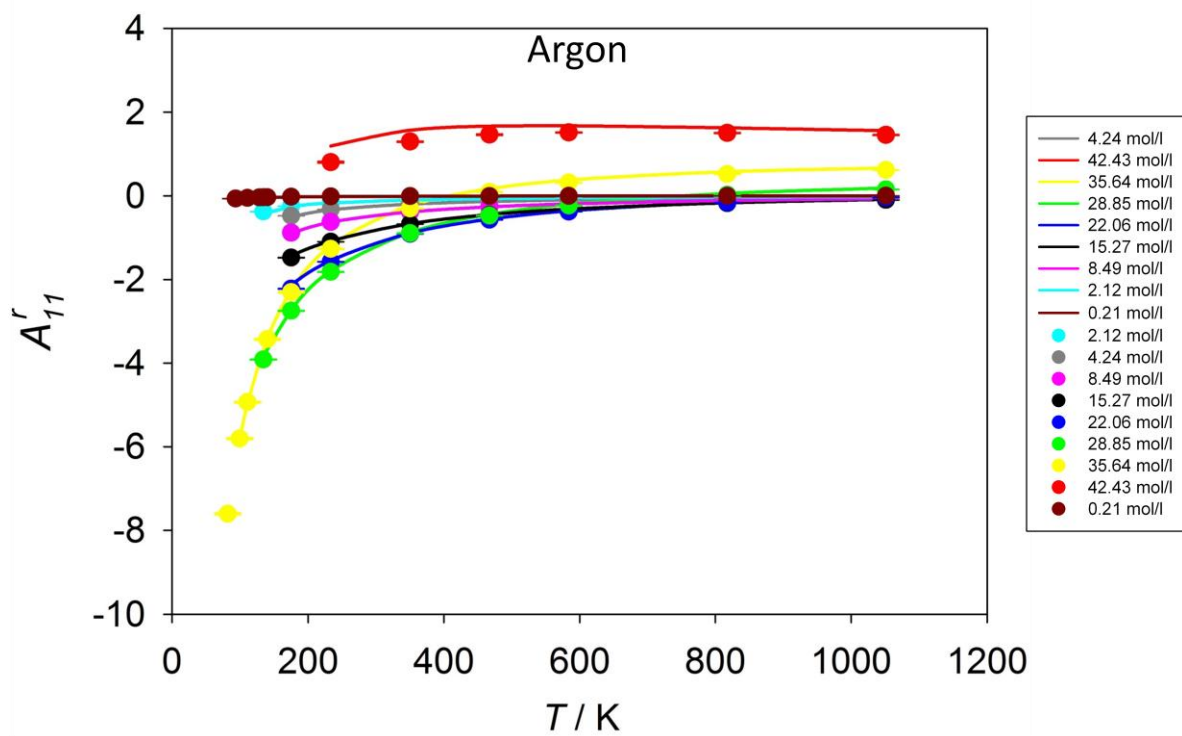
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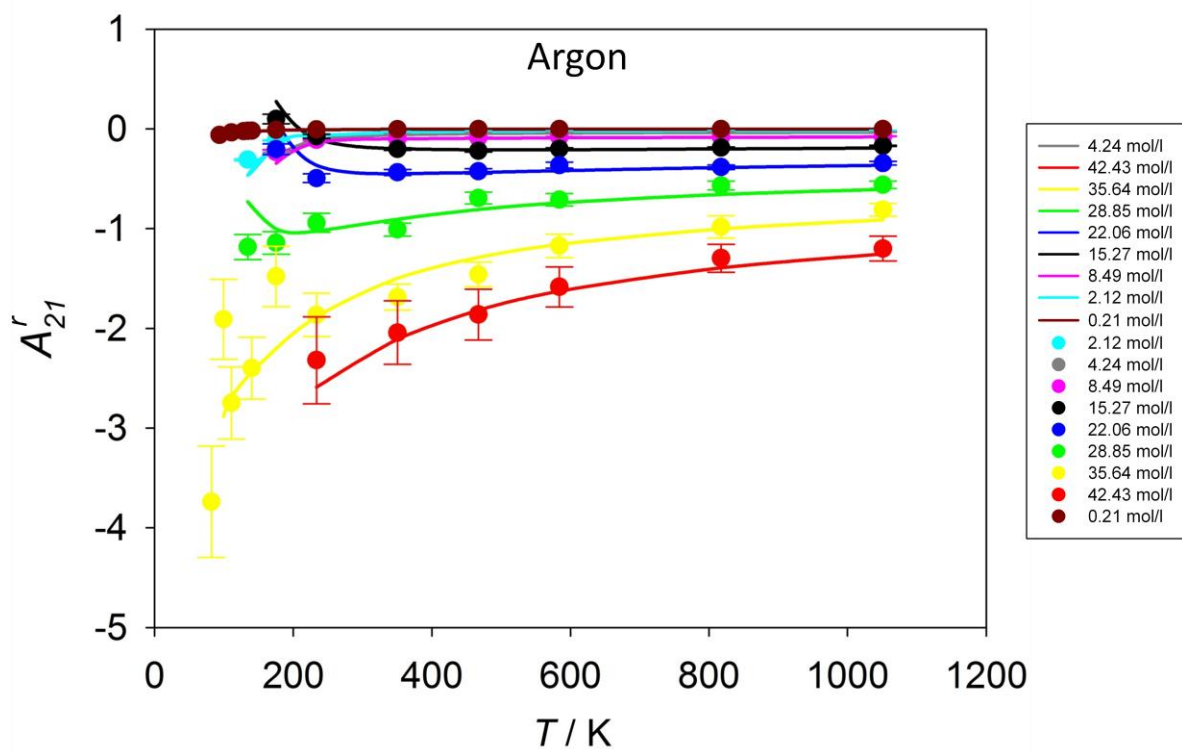
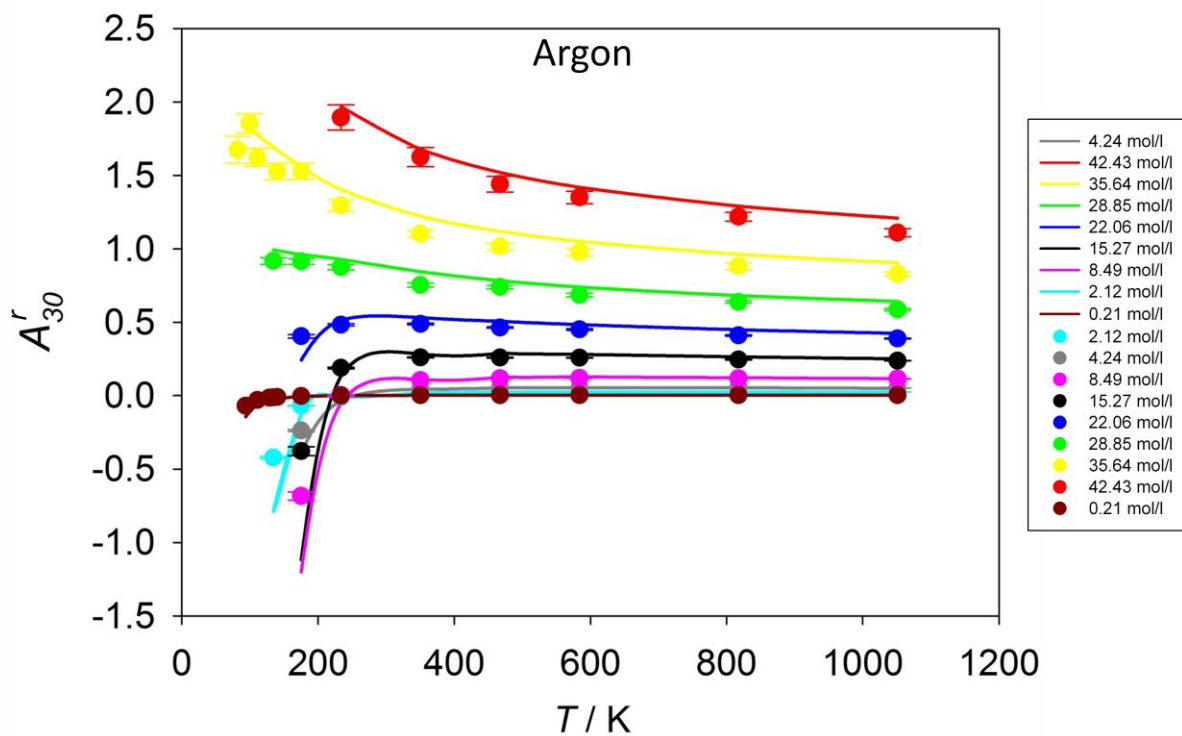
Comparison of residual Helmholtz energy derivatives (A_{mn}^r) from molecular simulation (symbols) with FEOS correlations (lines). Note that lines are absent outside the range of validity of FEOS correlations.

FEOS: J. Phys. Chem. Ref. Data, 28(3):779-850, 1999.
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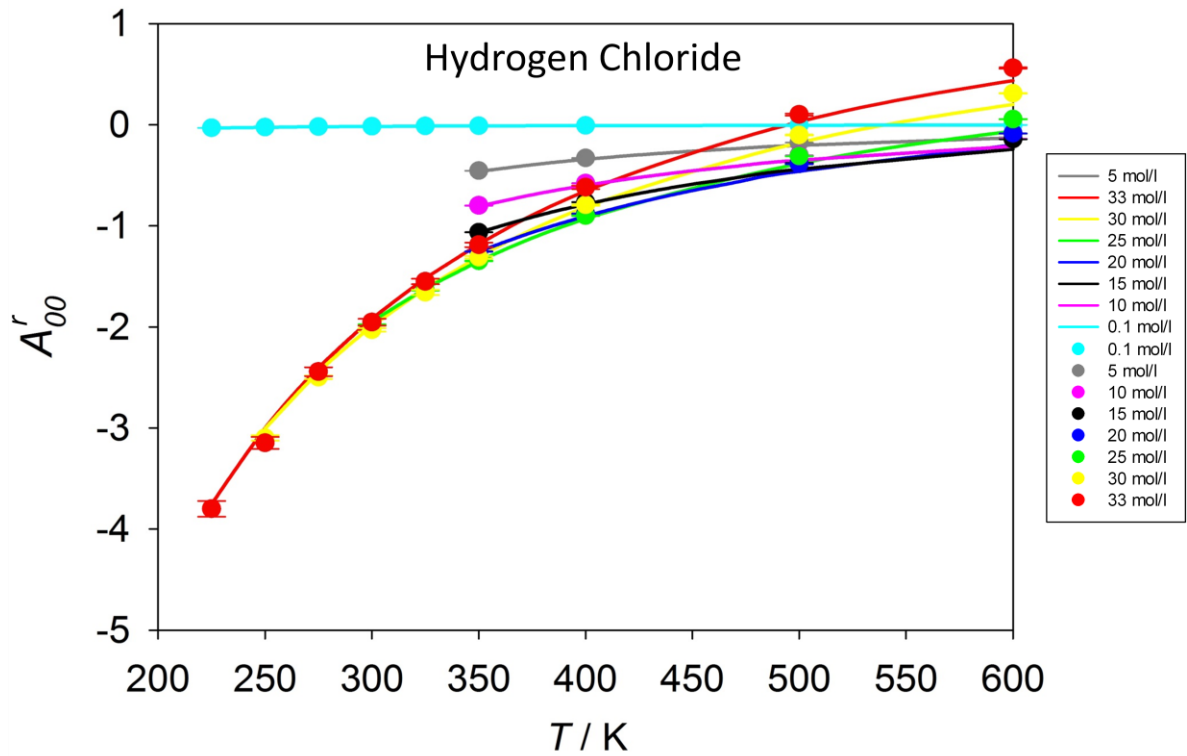




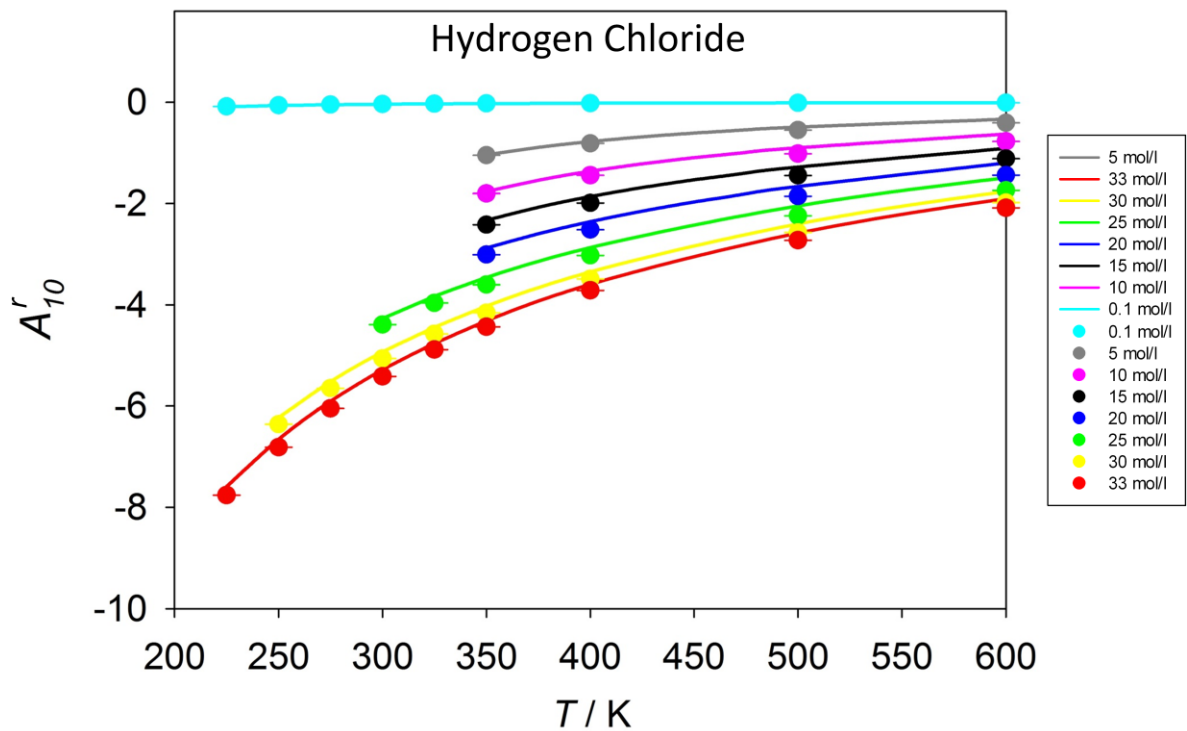


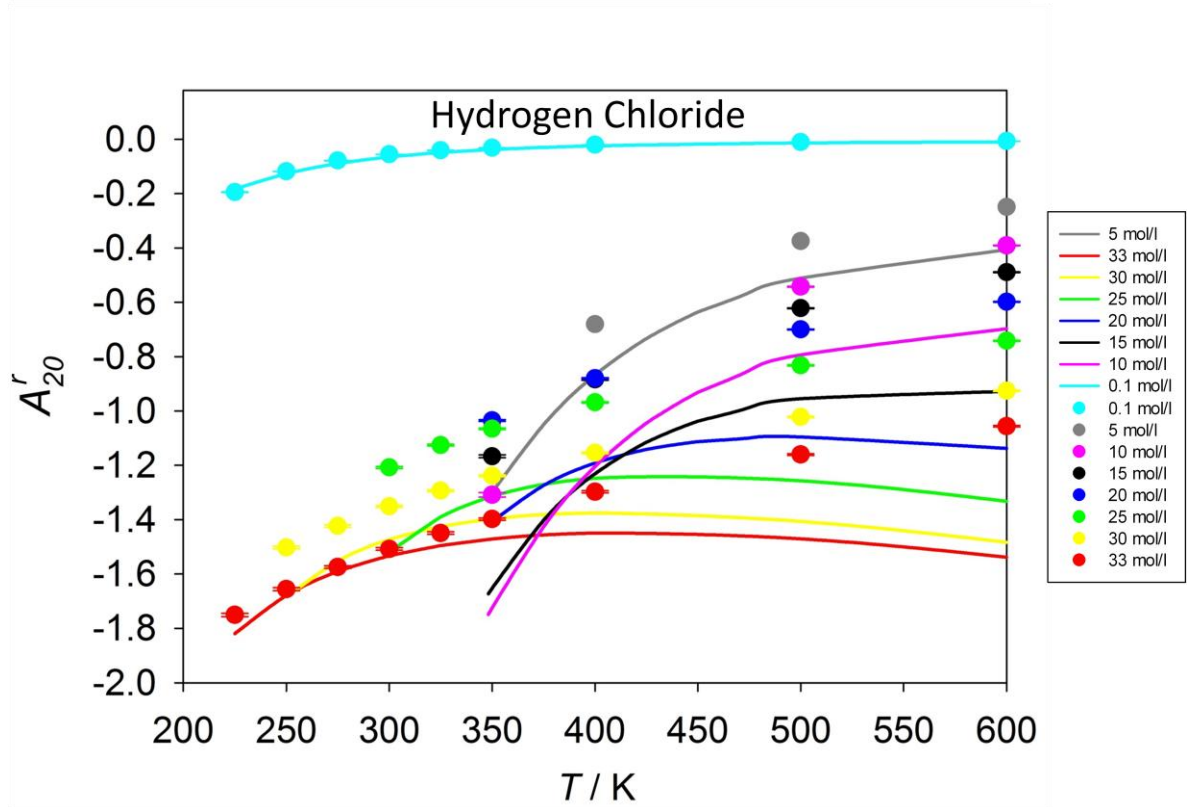
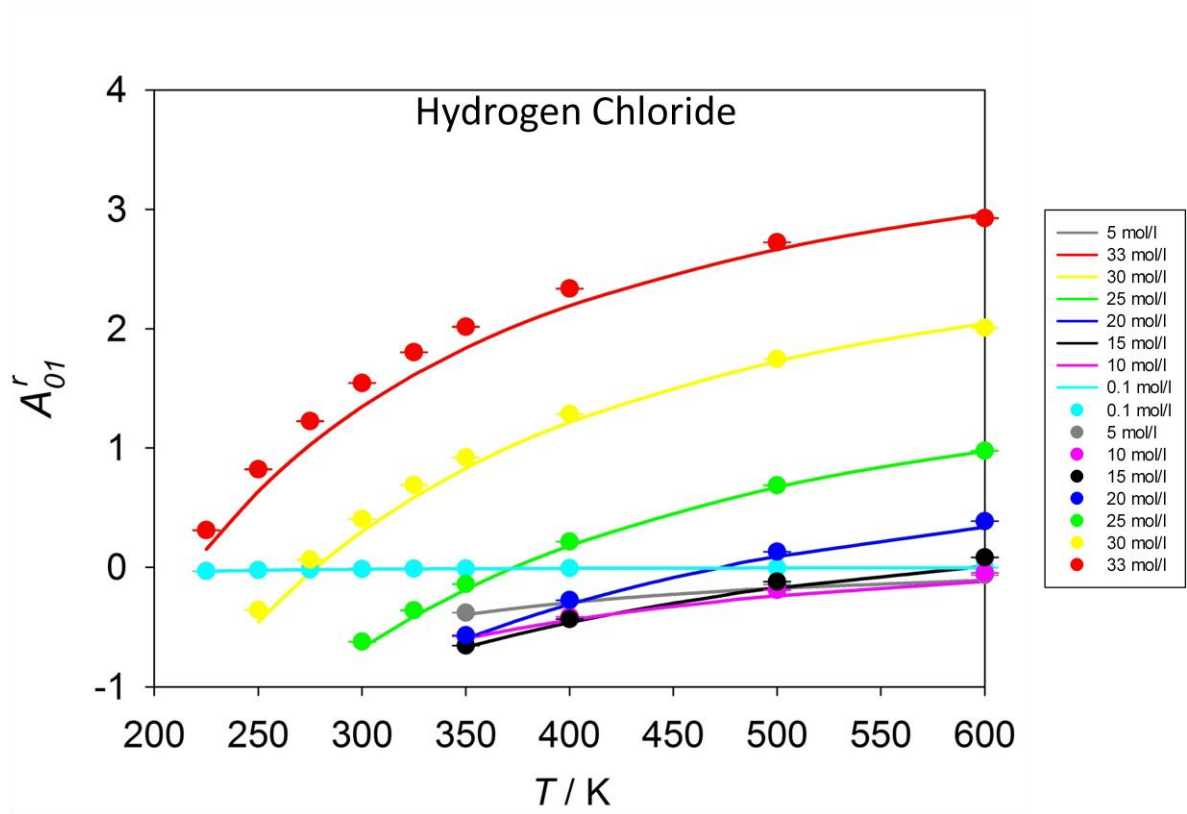


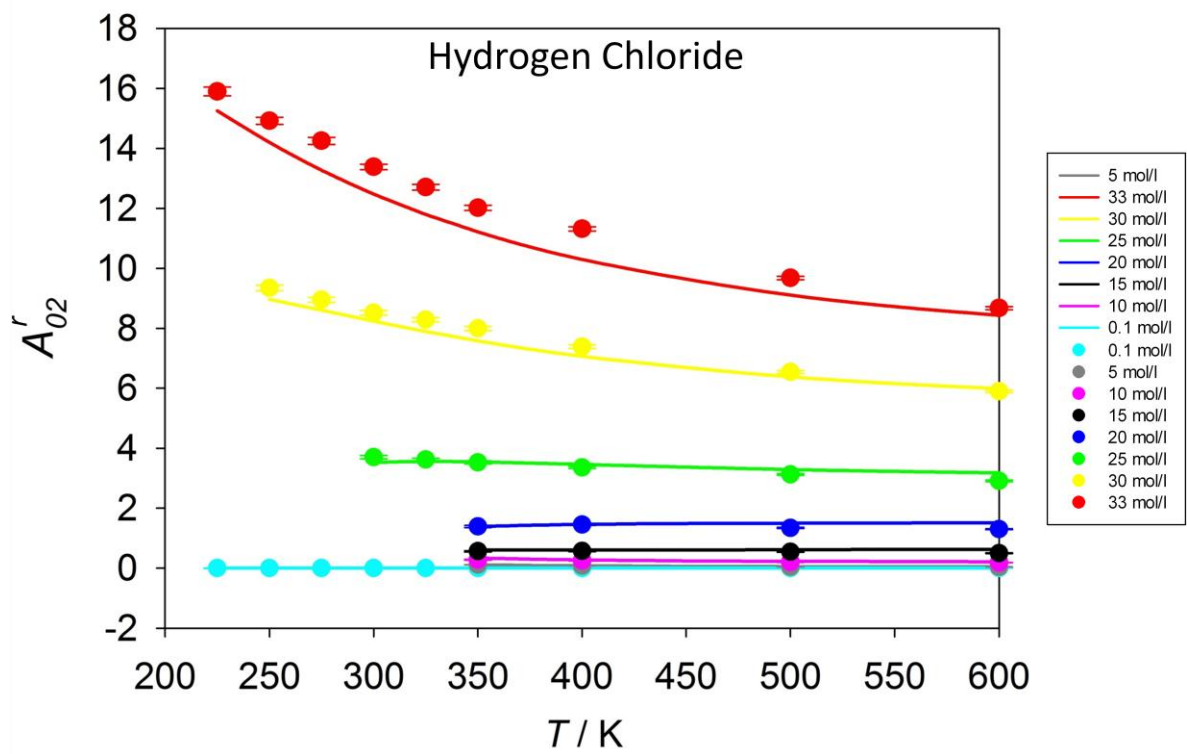
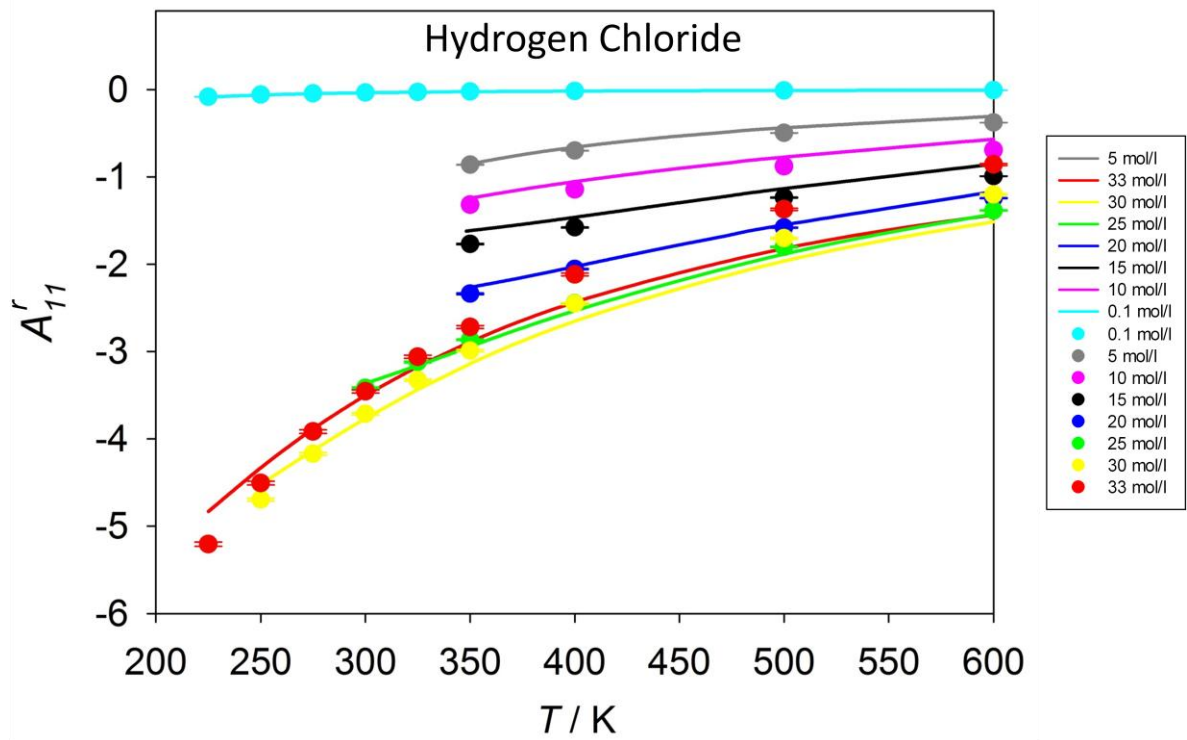
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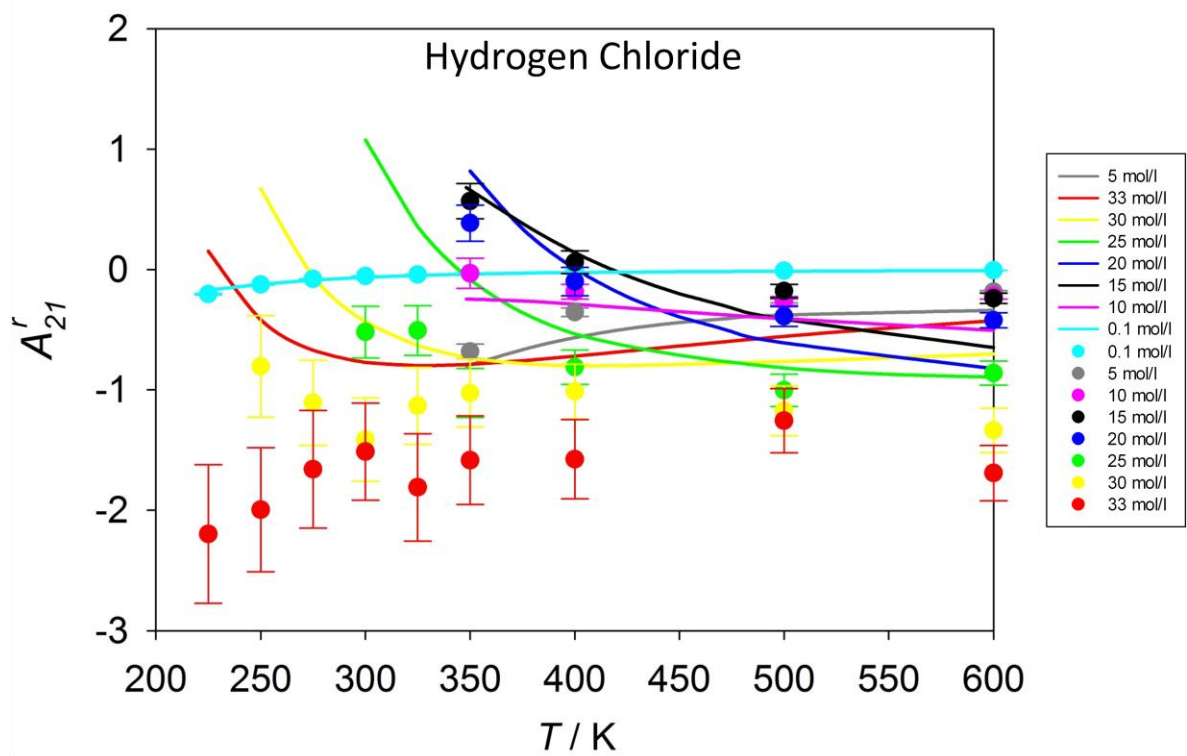
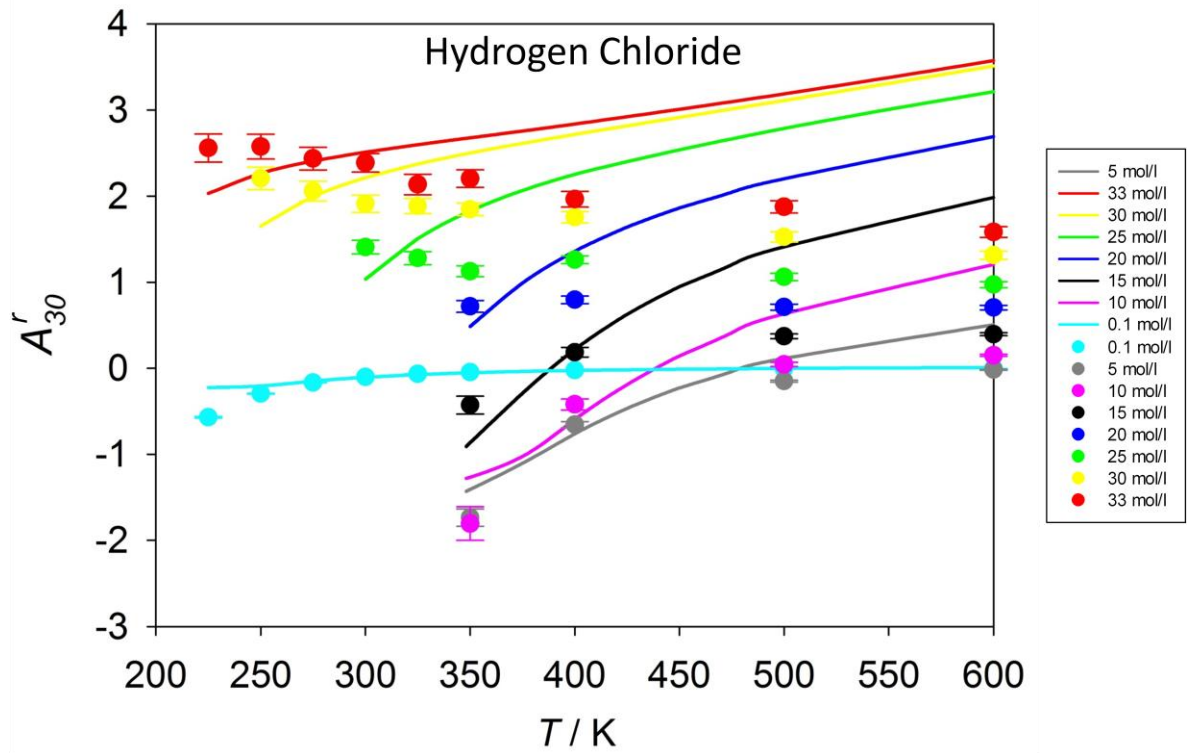


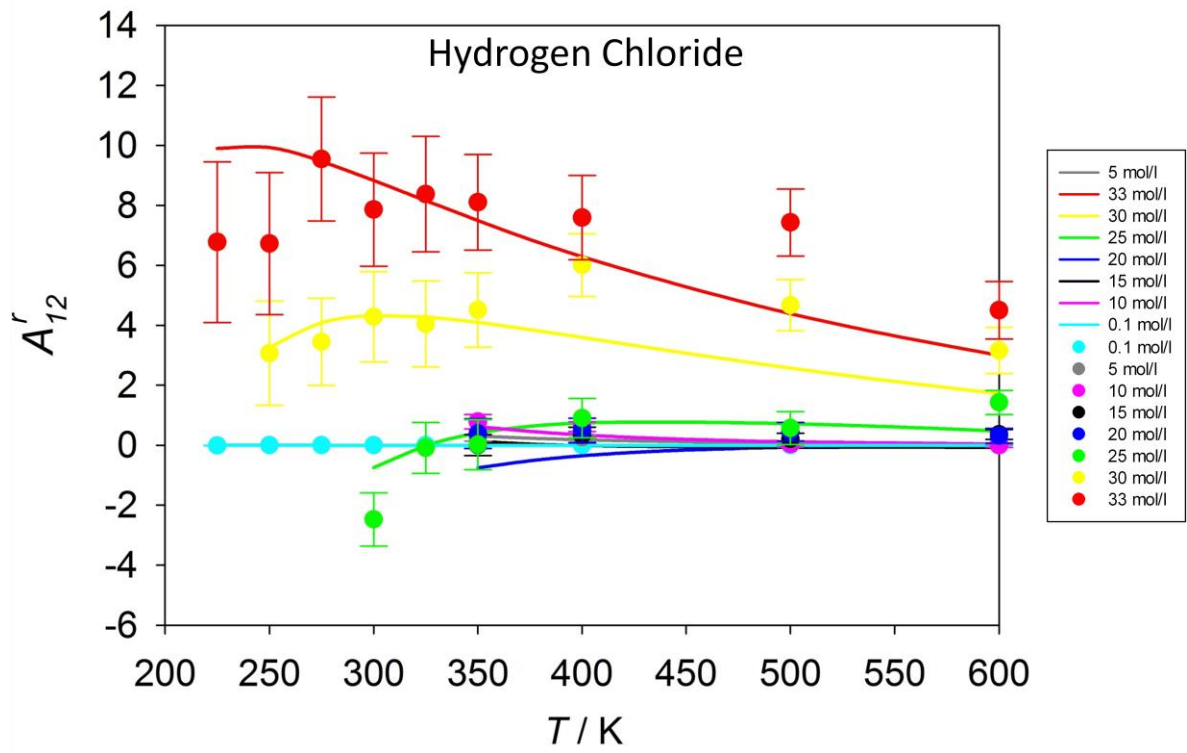
*M. Thol, Entwicklung einer funktionalen Form für Zustandsgleichungen für polare und schwach assoziierende Fluide, diploma thesis, Ruhr-University Bochum (2010).

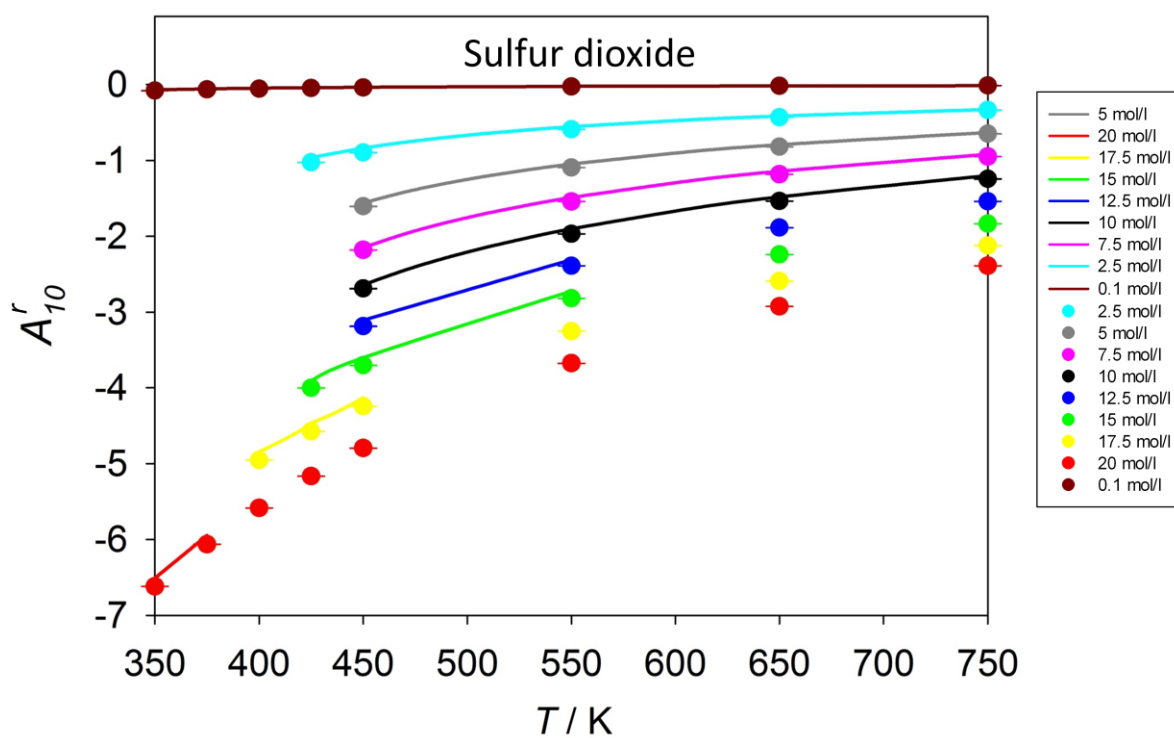
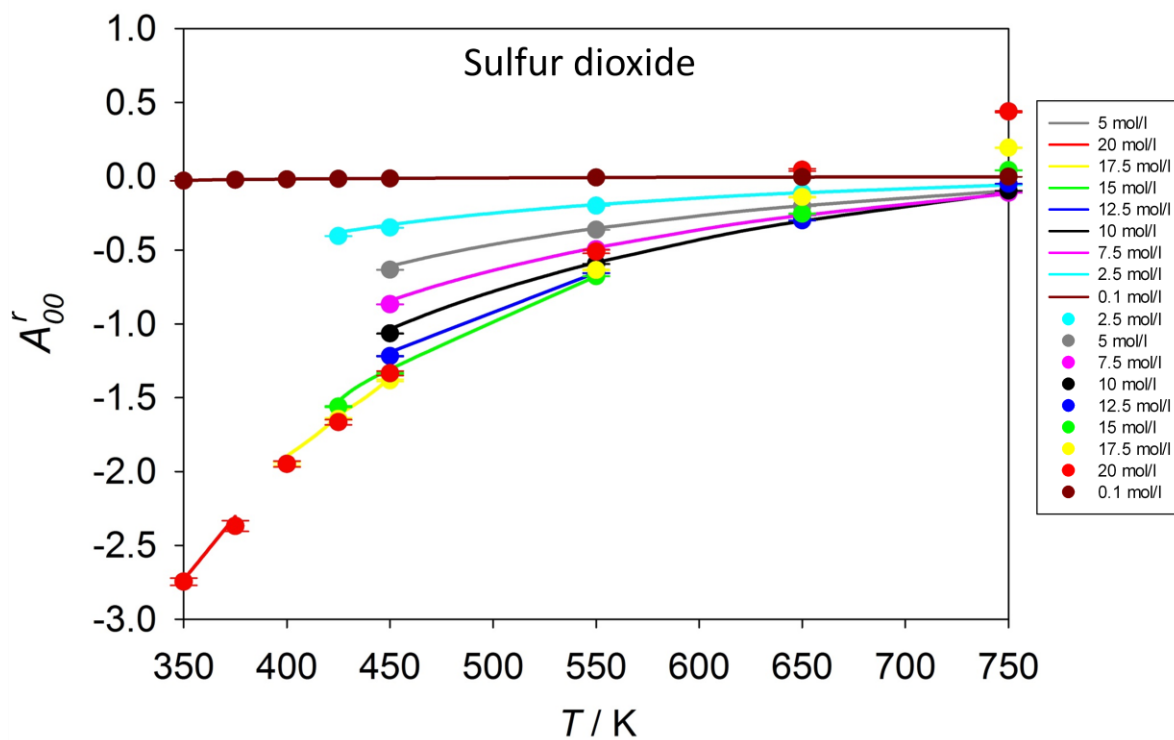


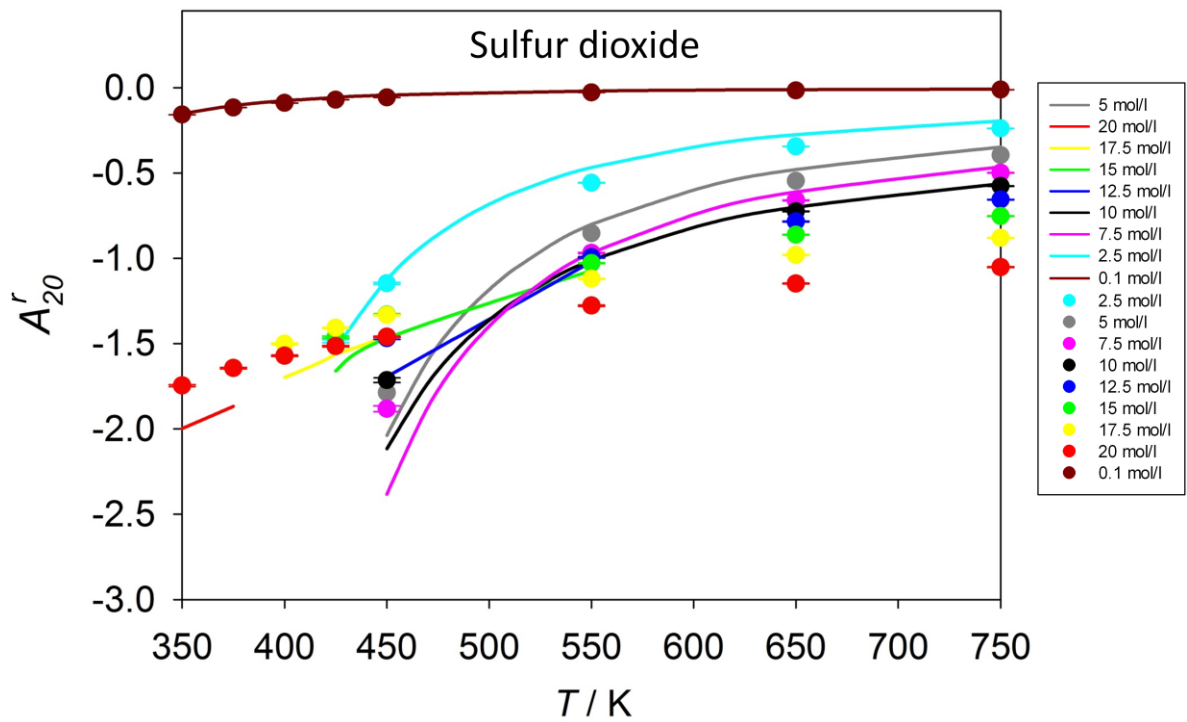
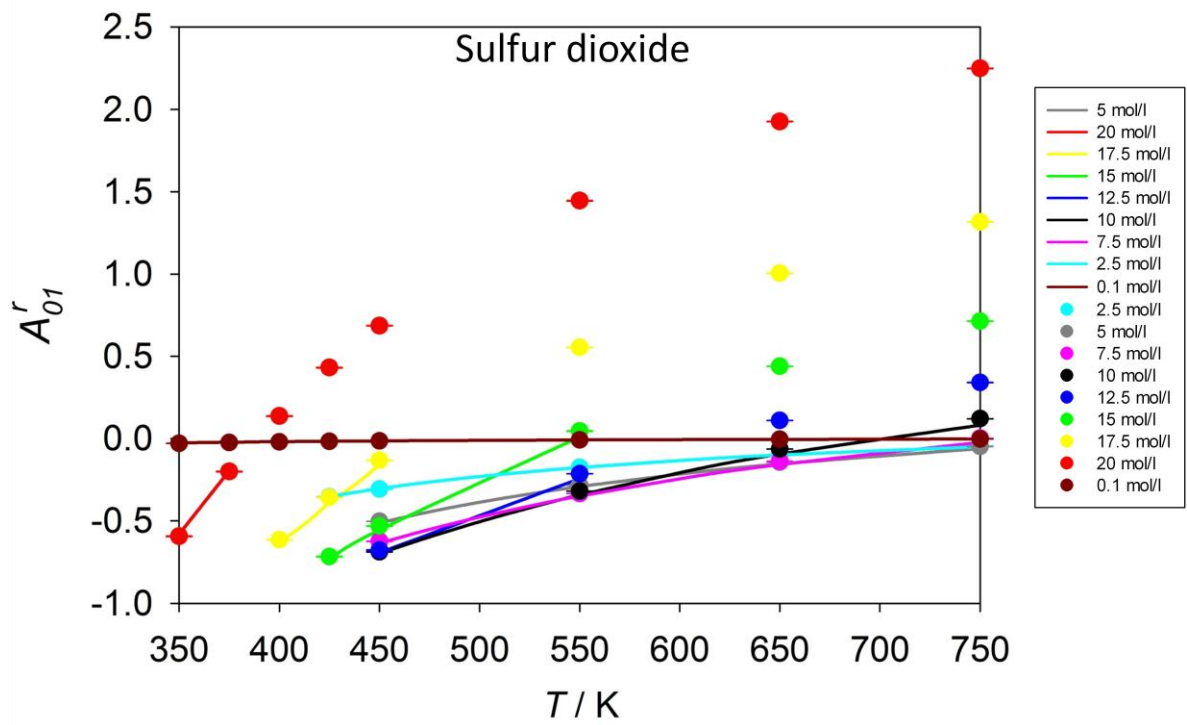


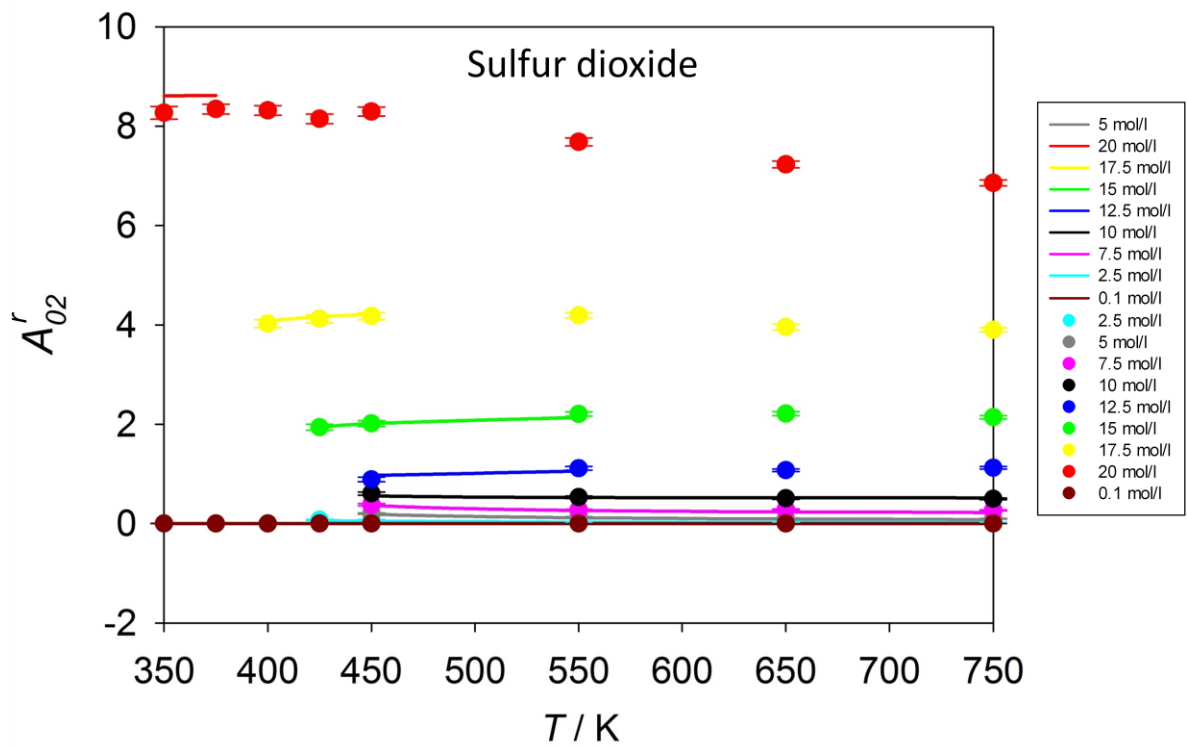
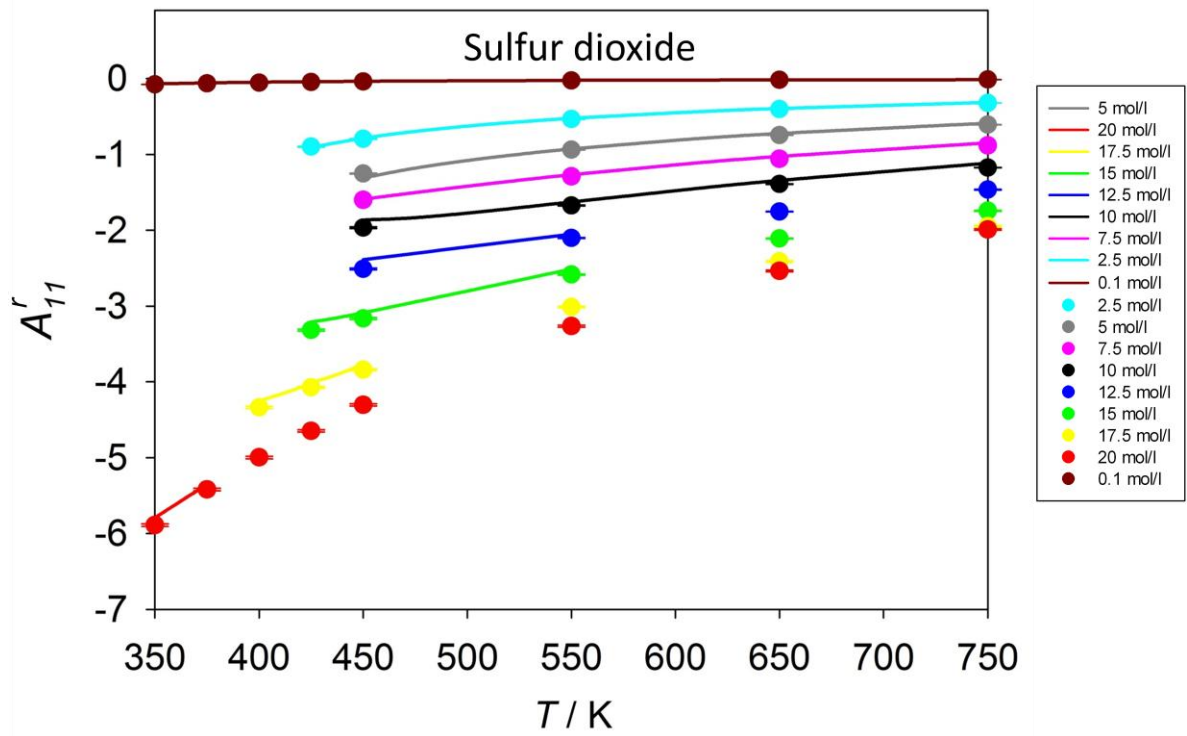


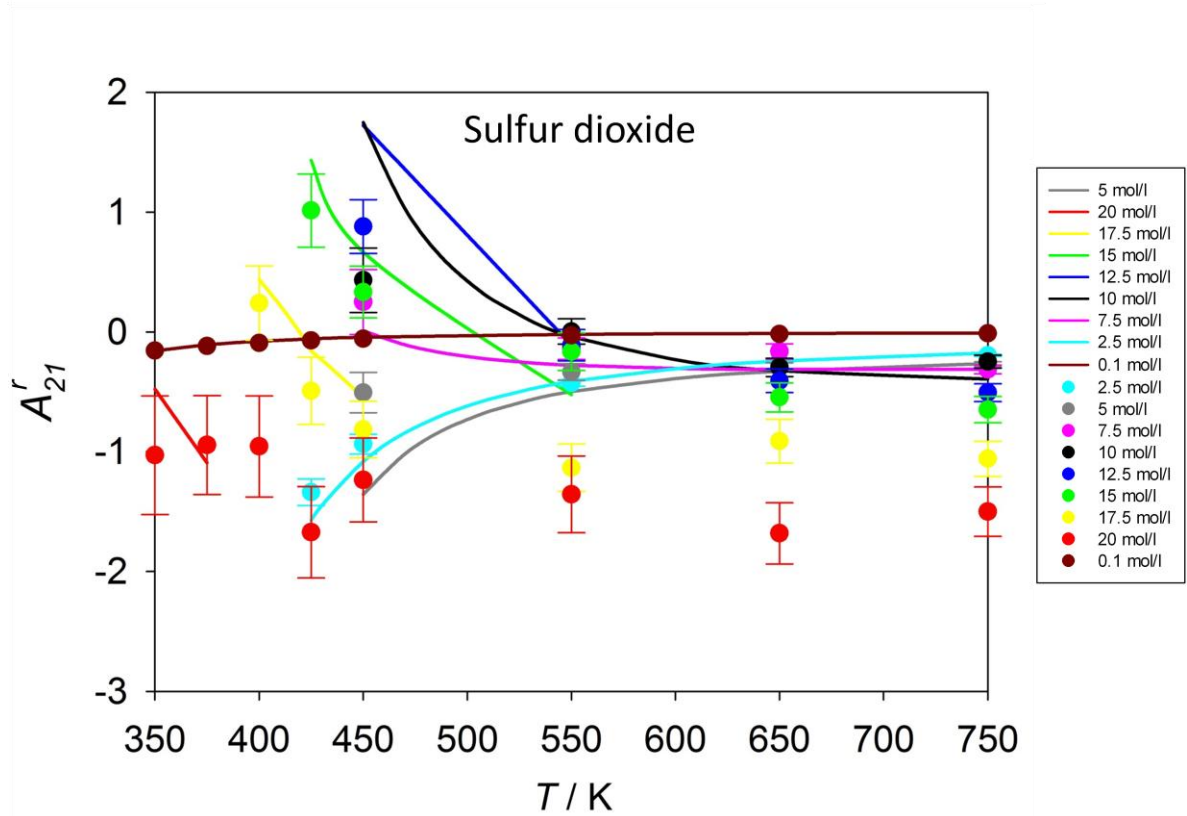
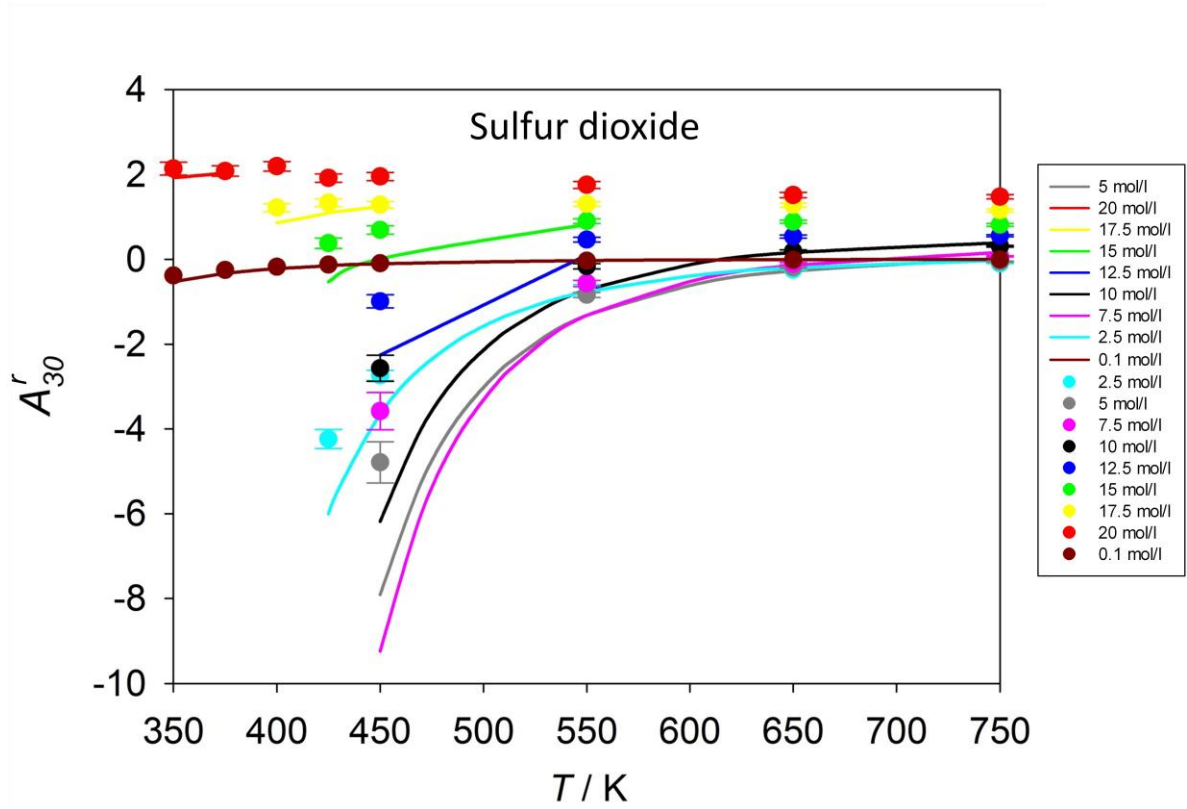




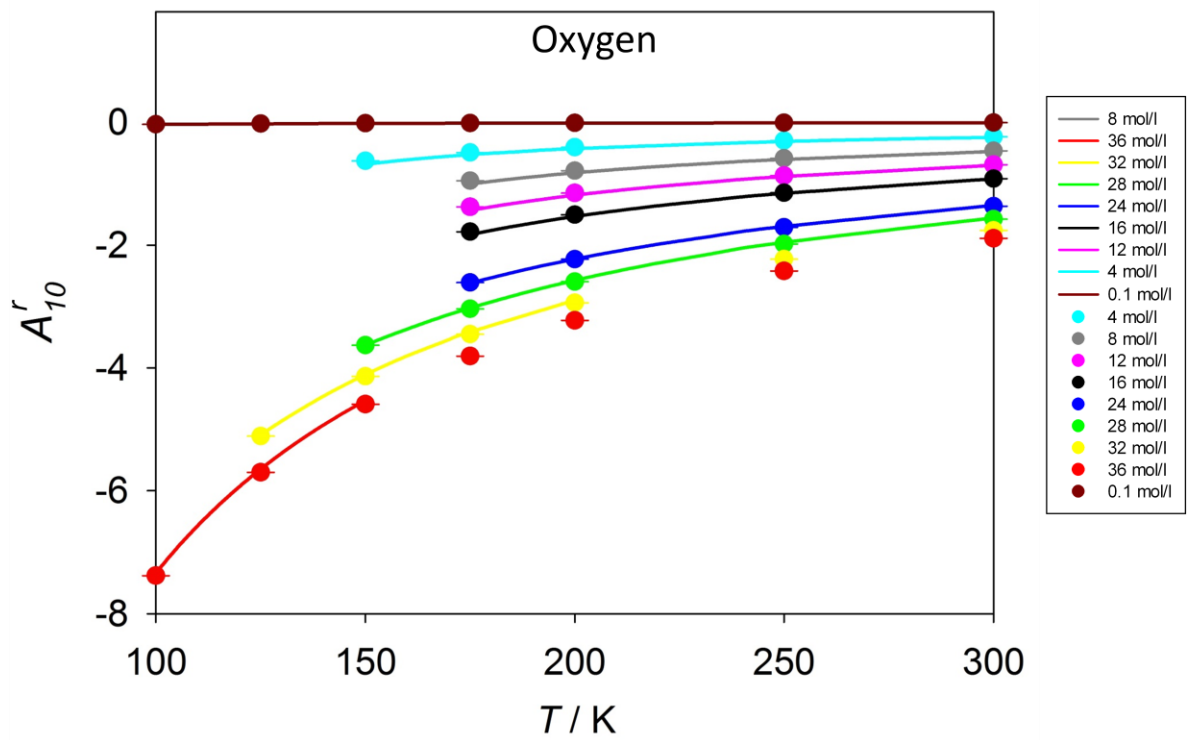
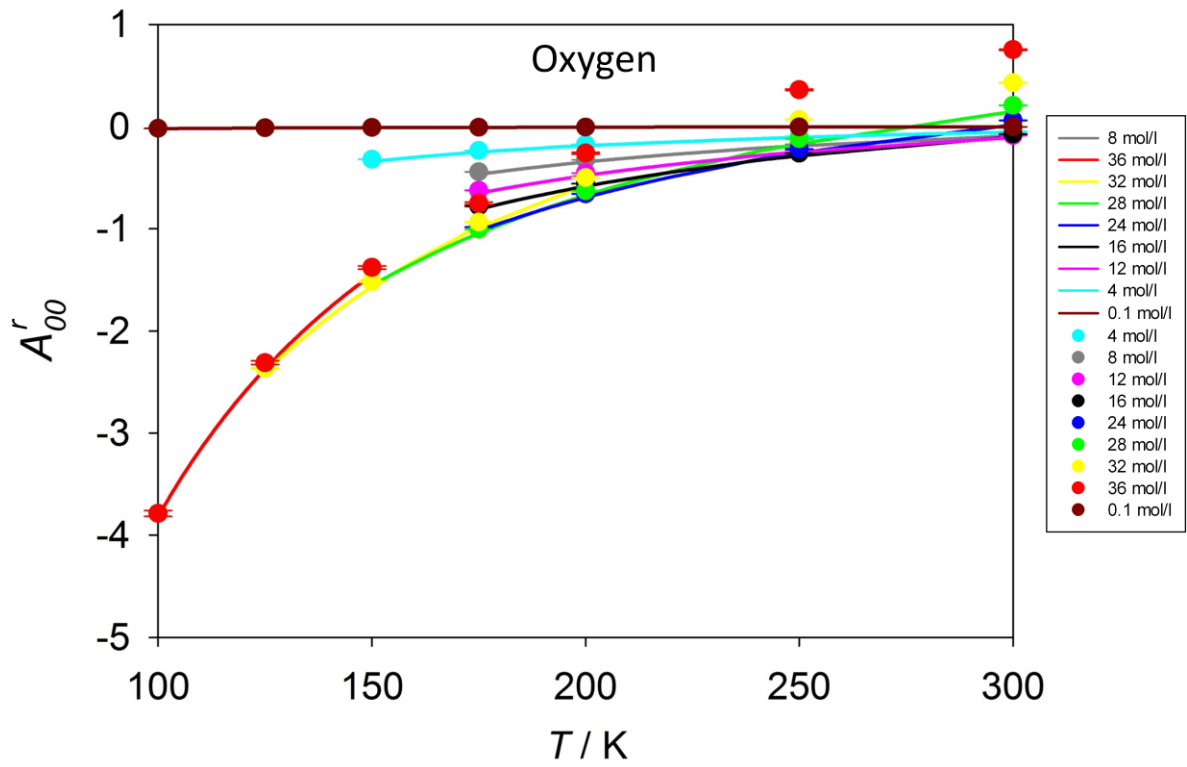


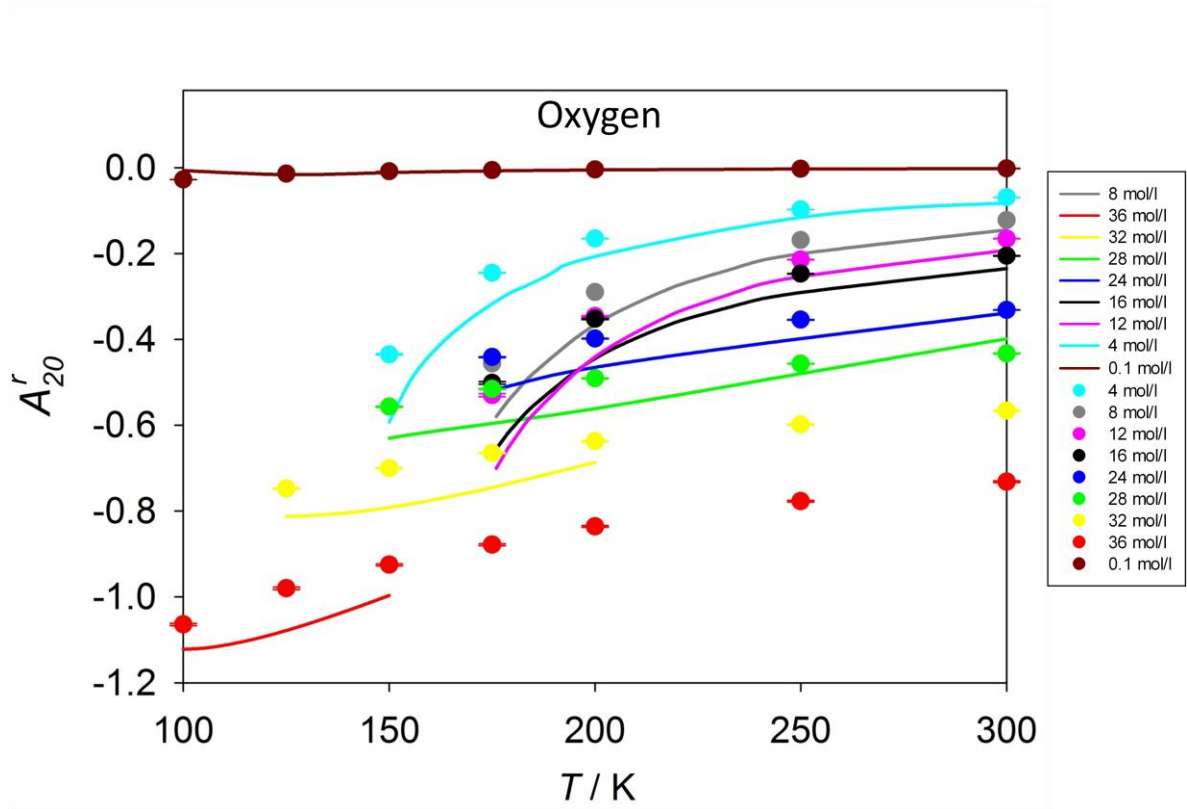
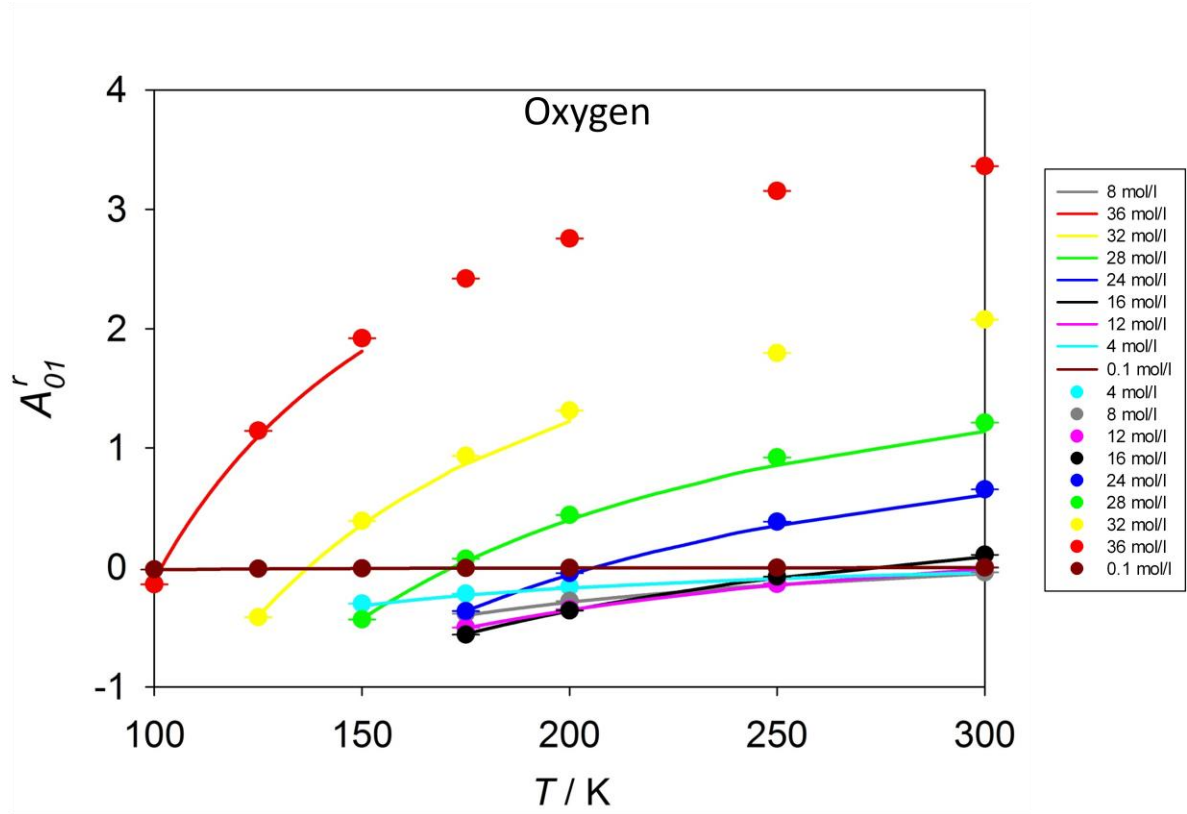


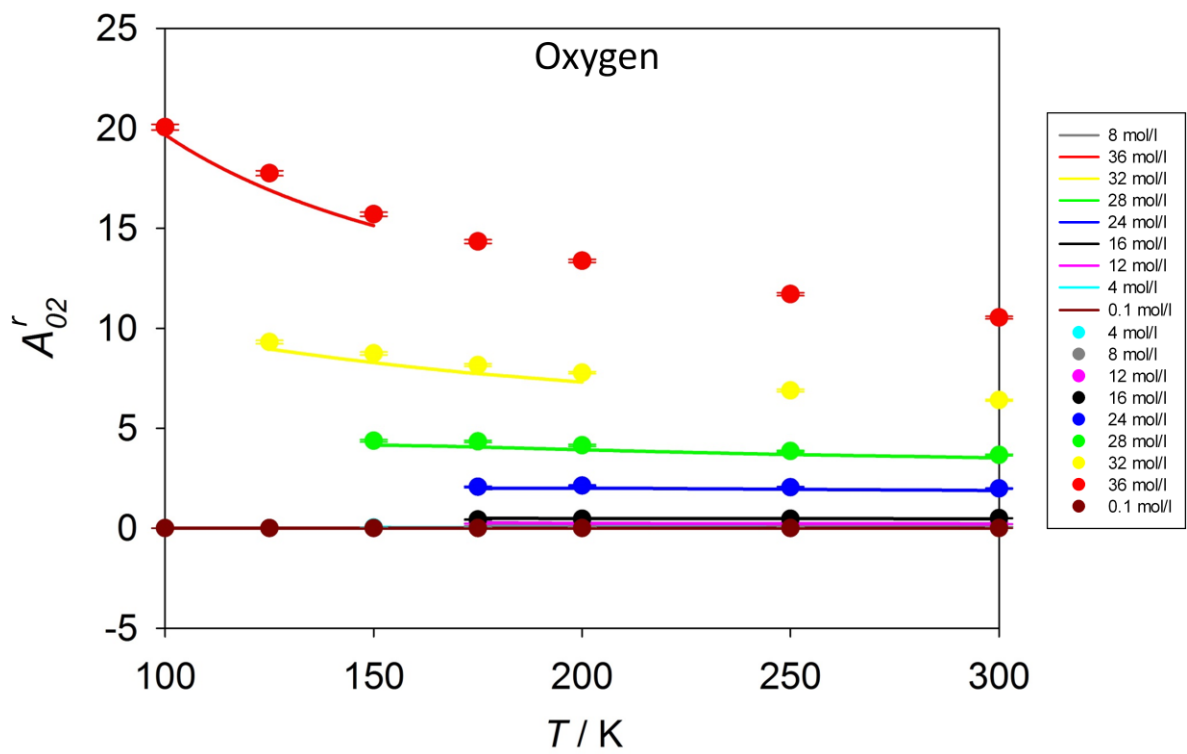
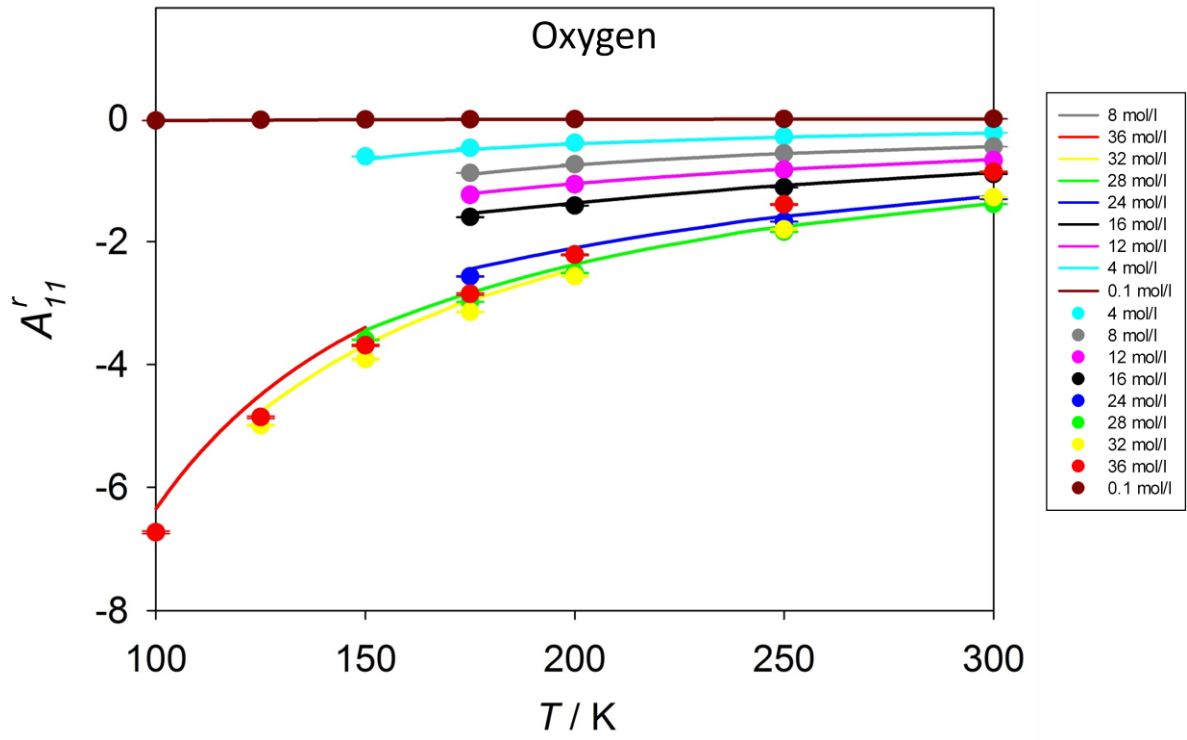


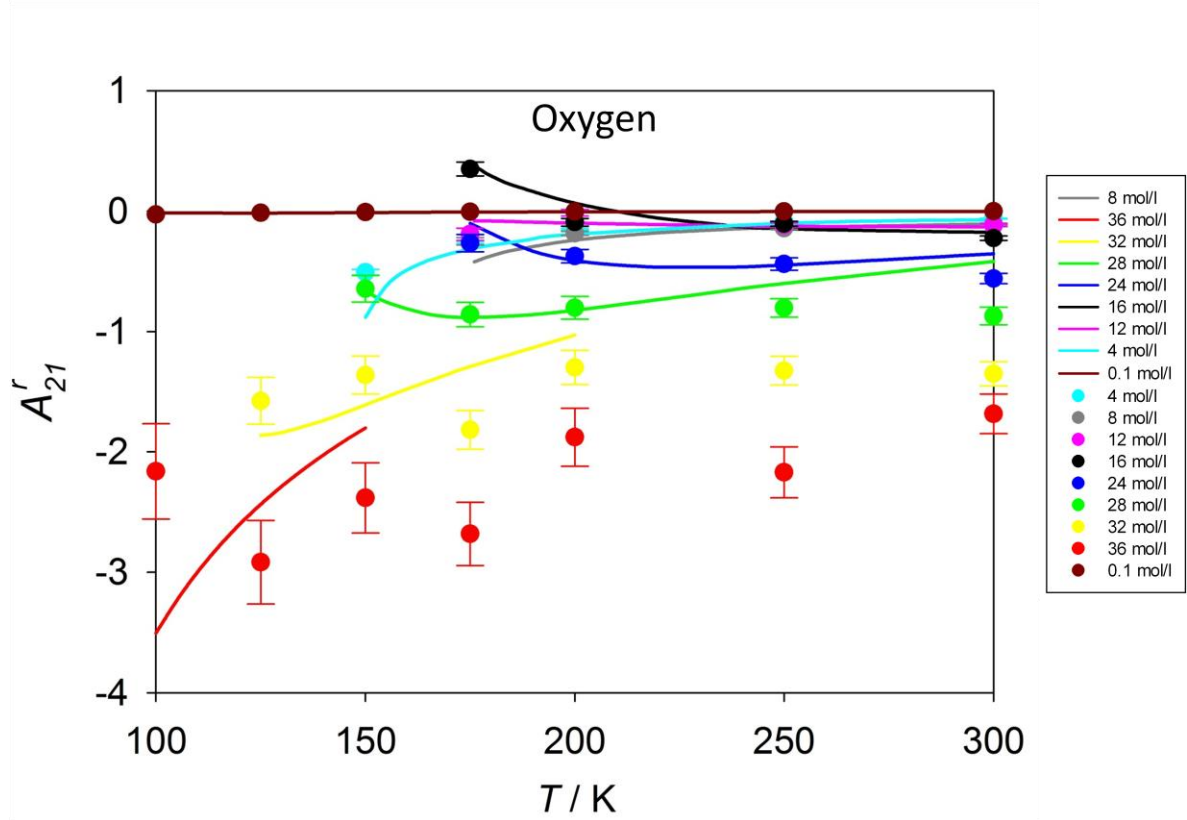
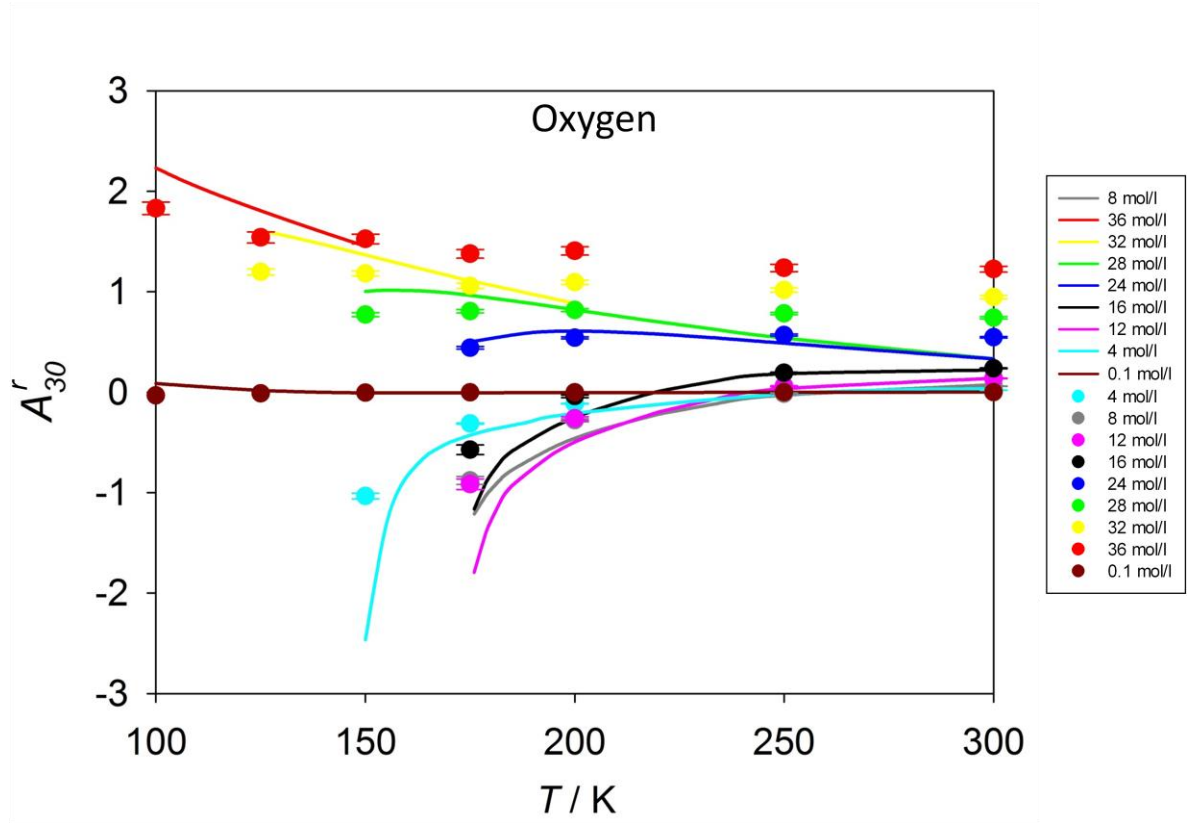


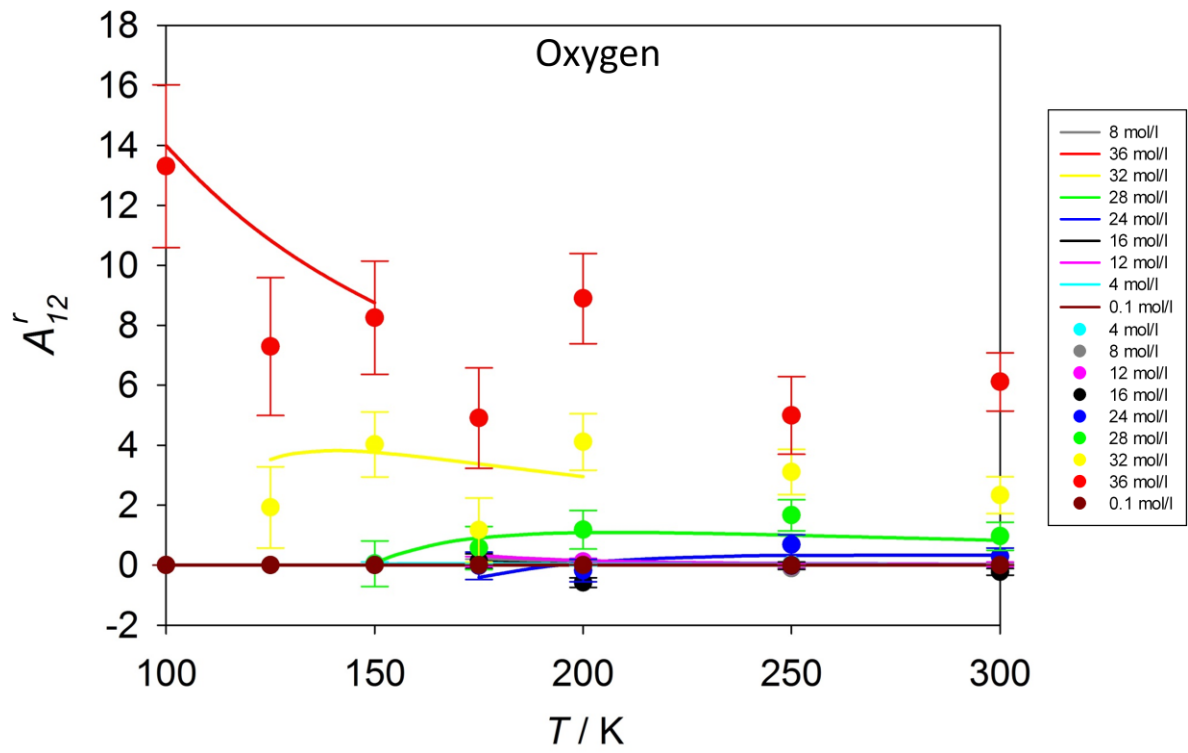
FEOS: Fluid Phase Equilibria, 19:175-200, 1985.
Interaction model: J. Phys. Chem. B, 105: 12126-12133, 2001.

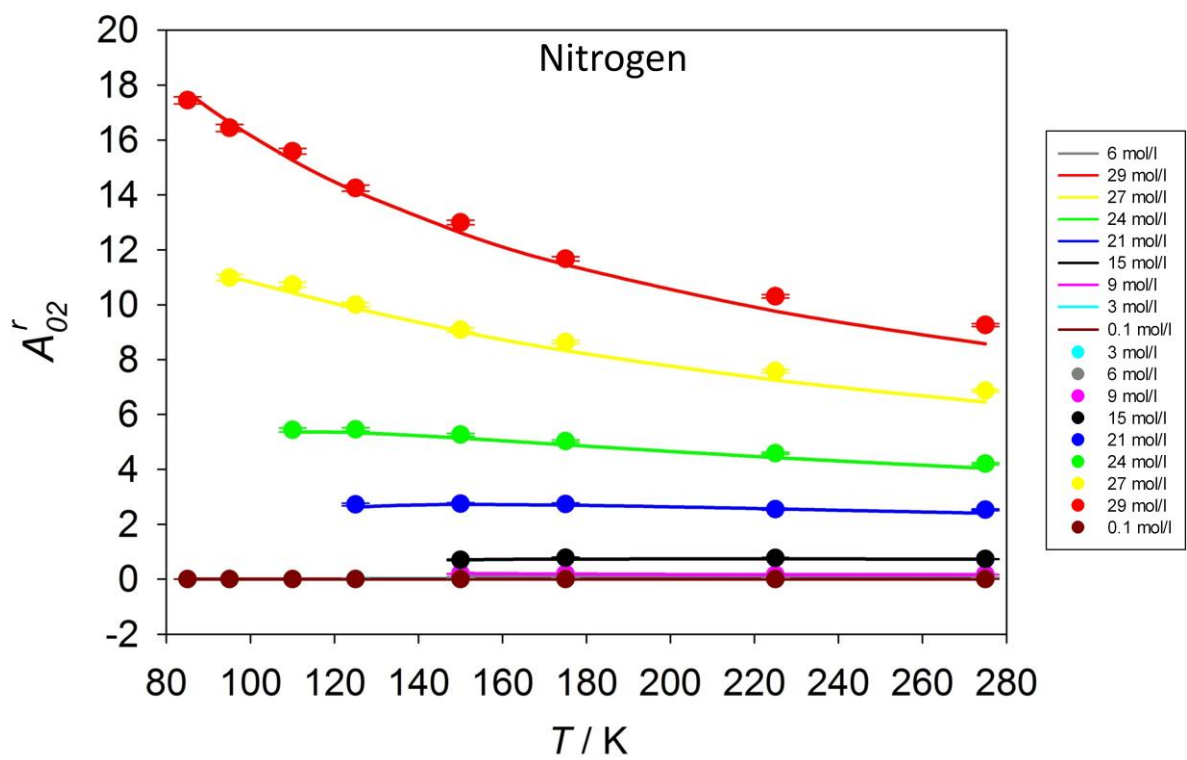
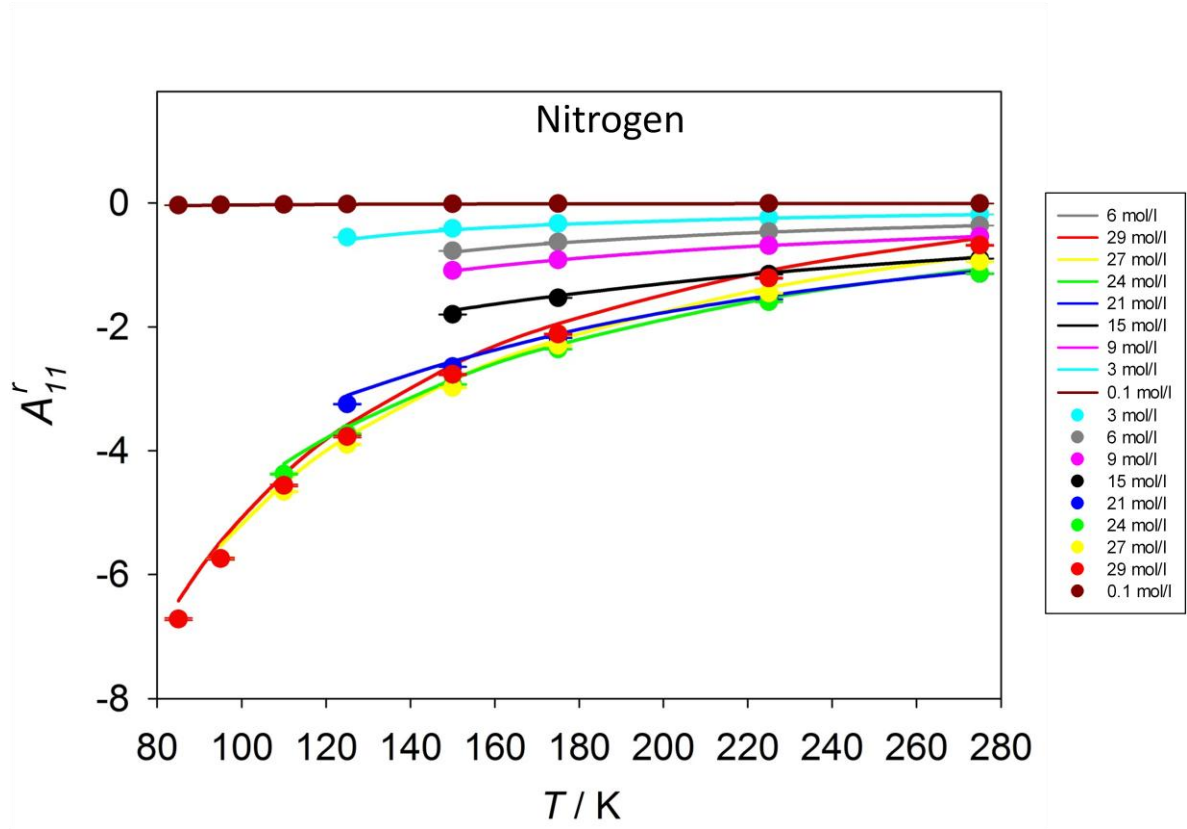


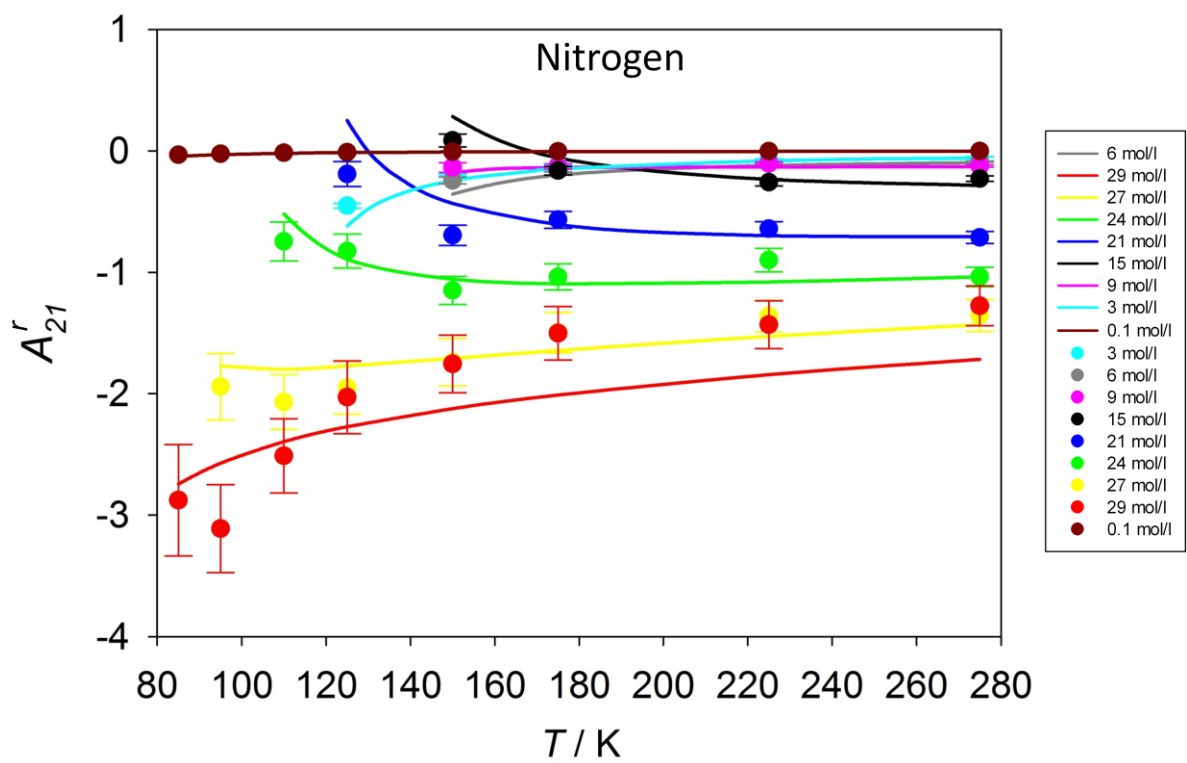
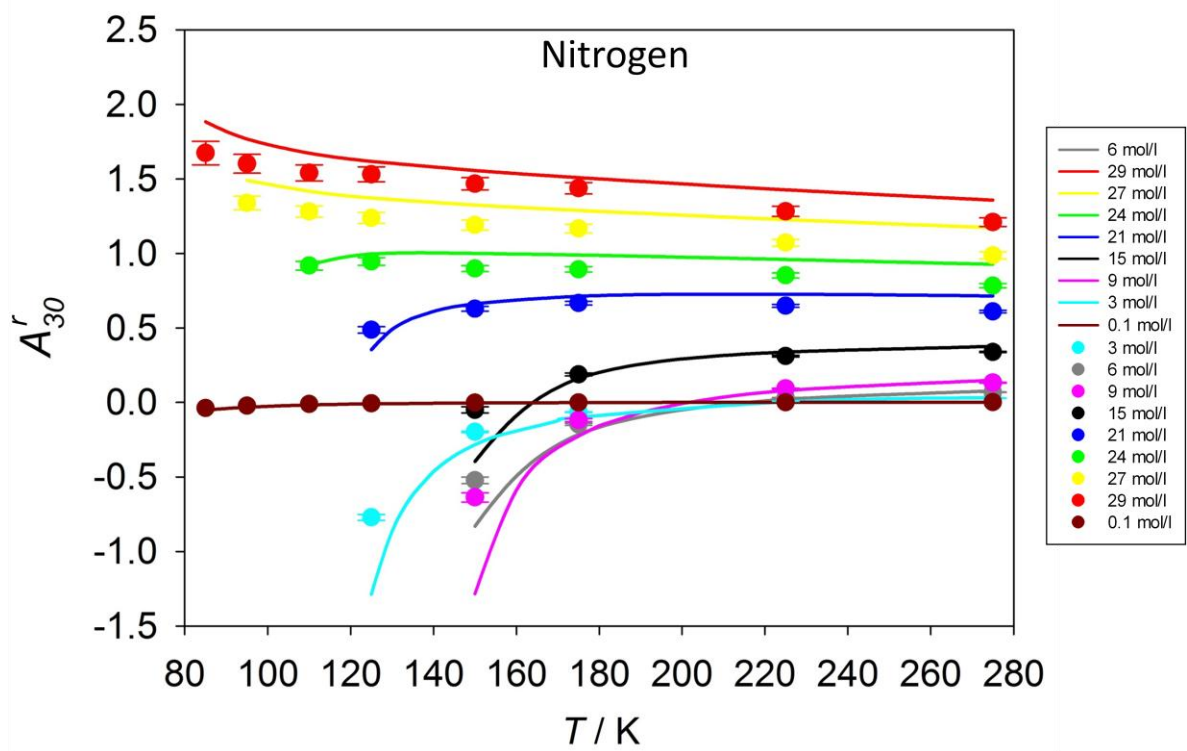


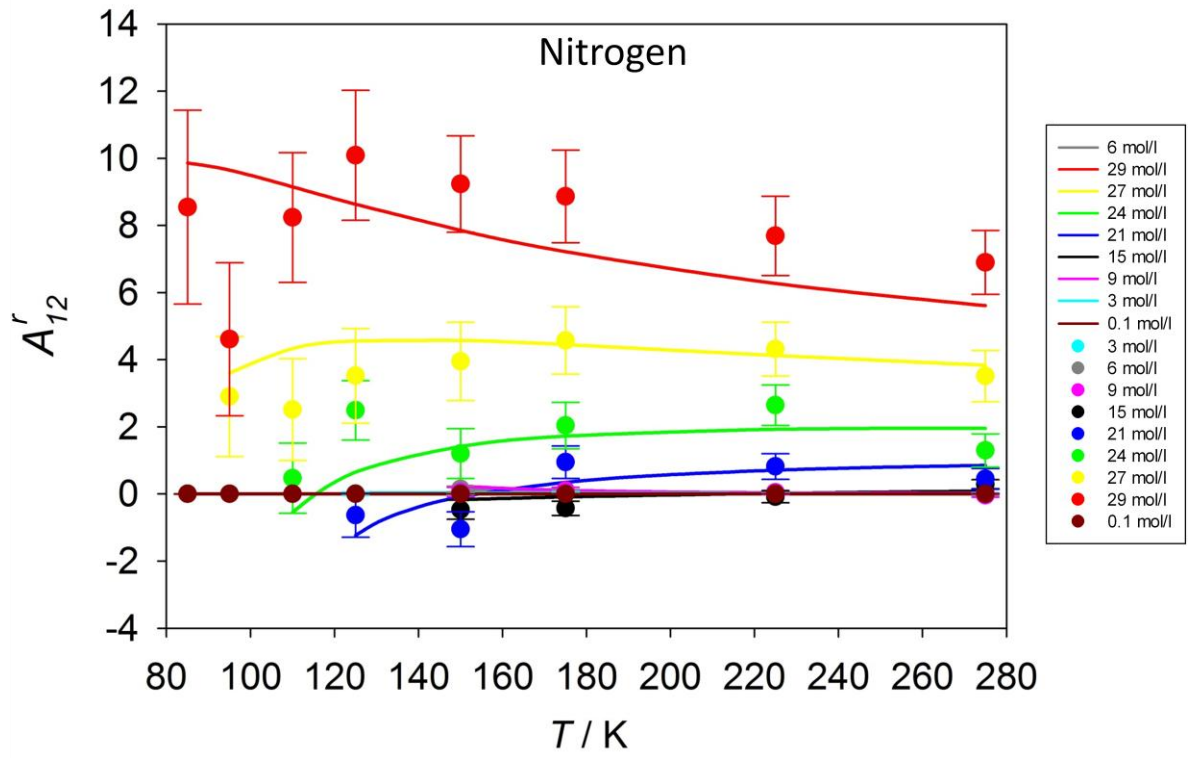






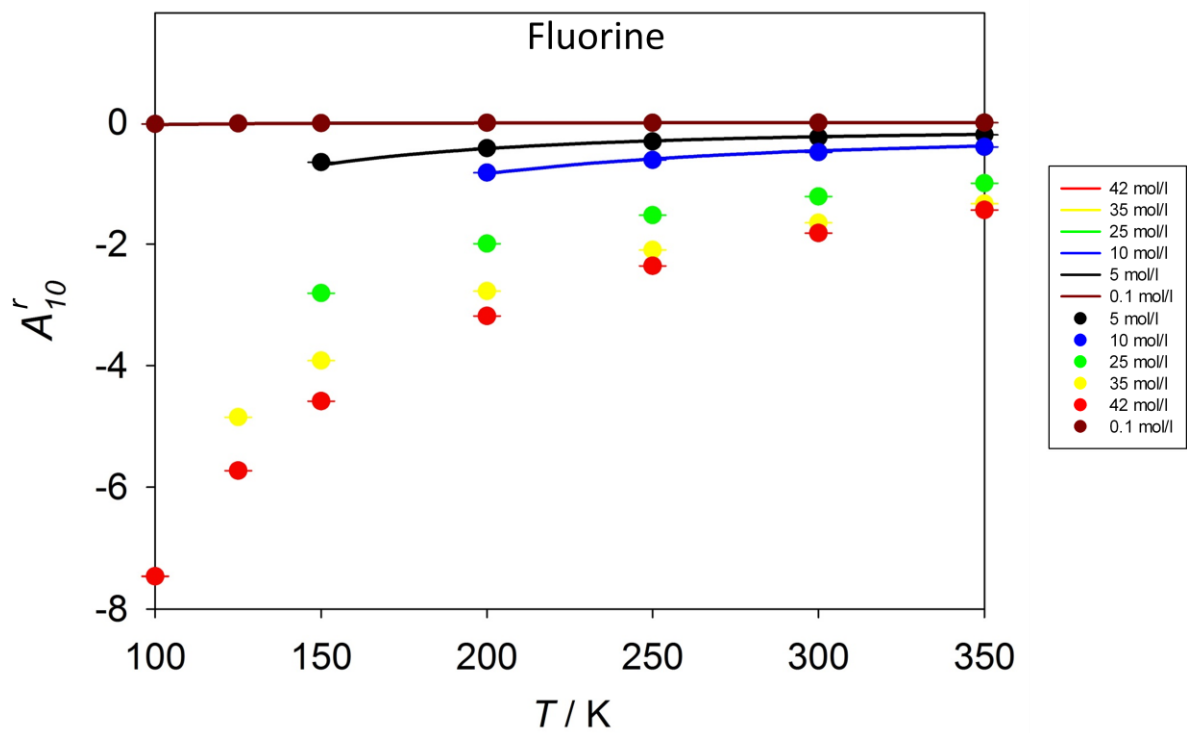
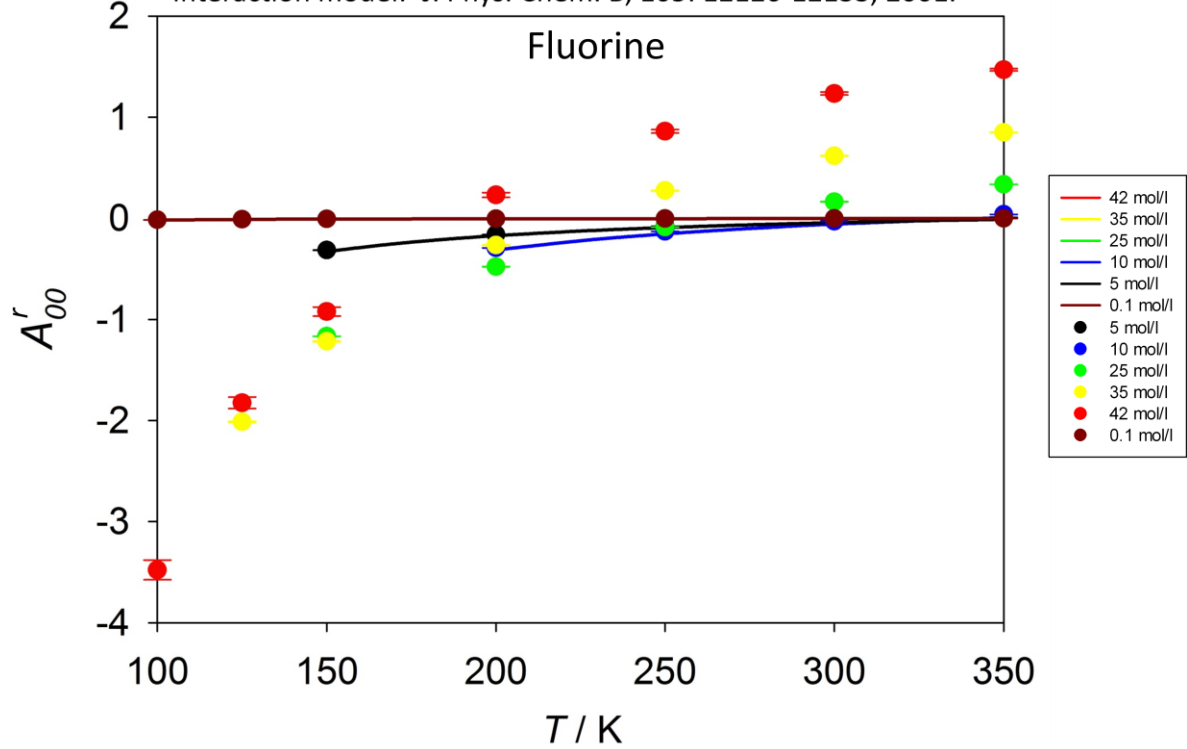


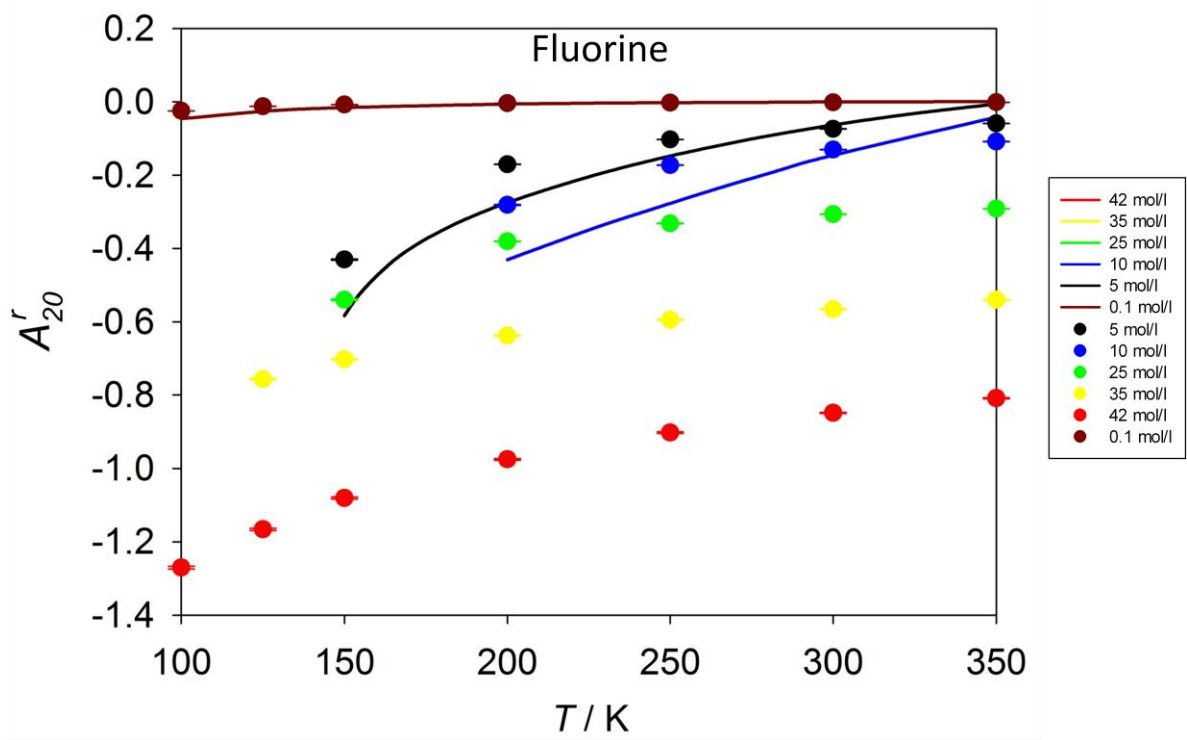
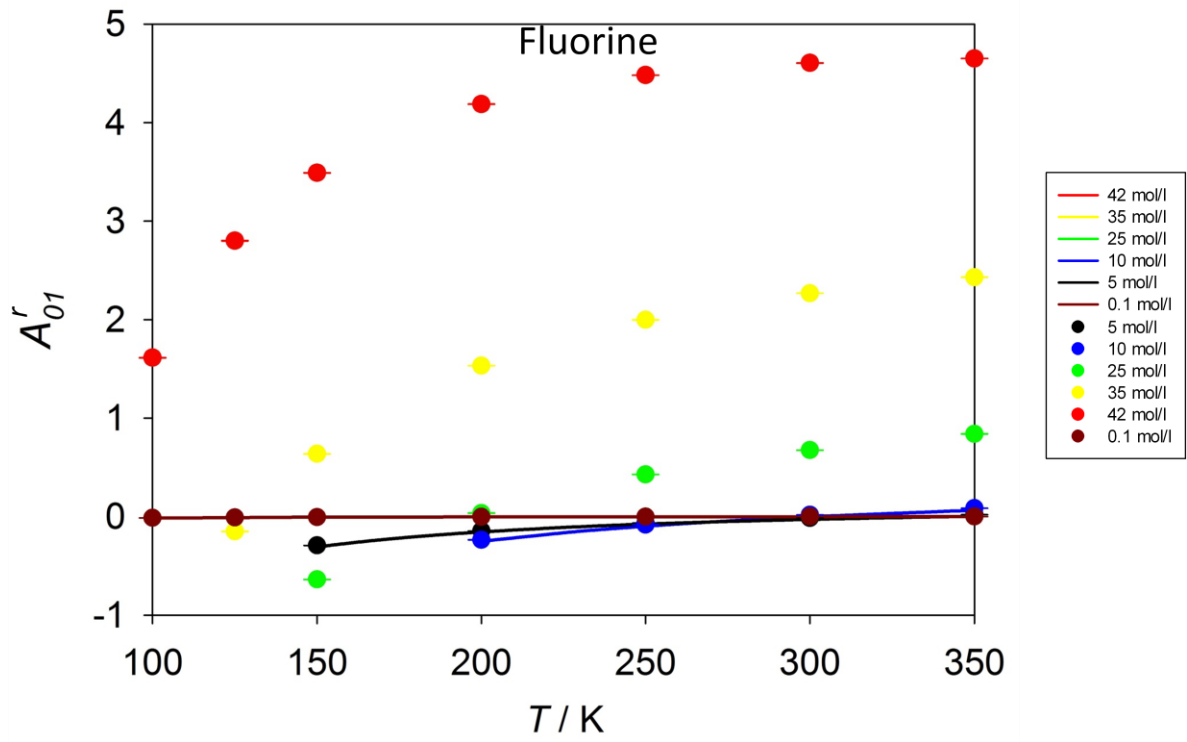


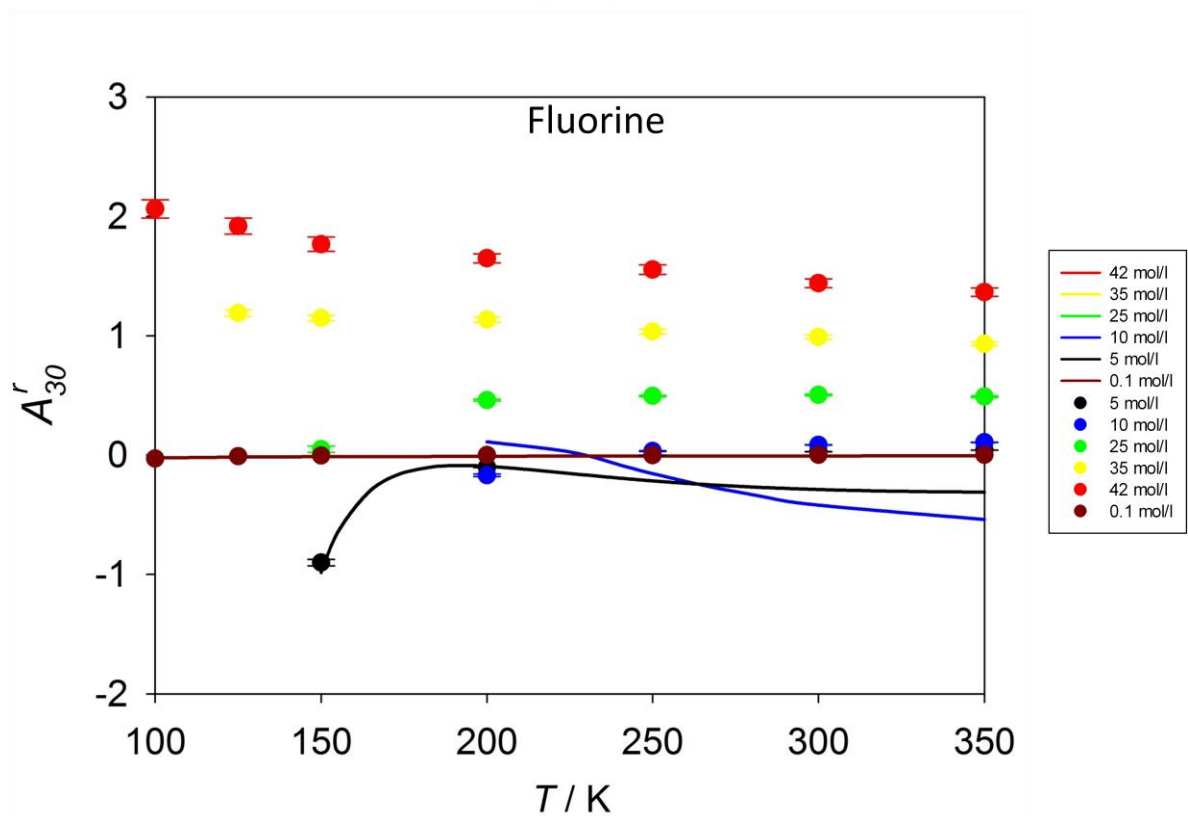
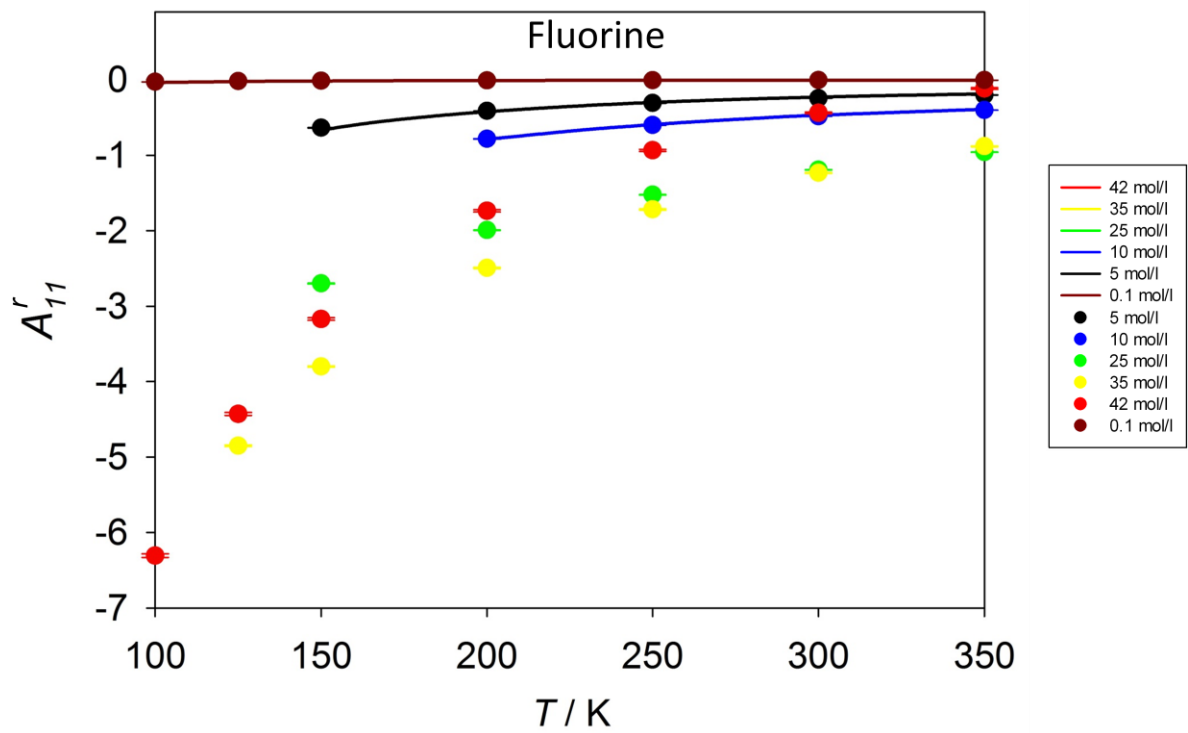


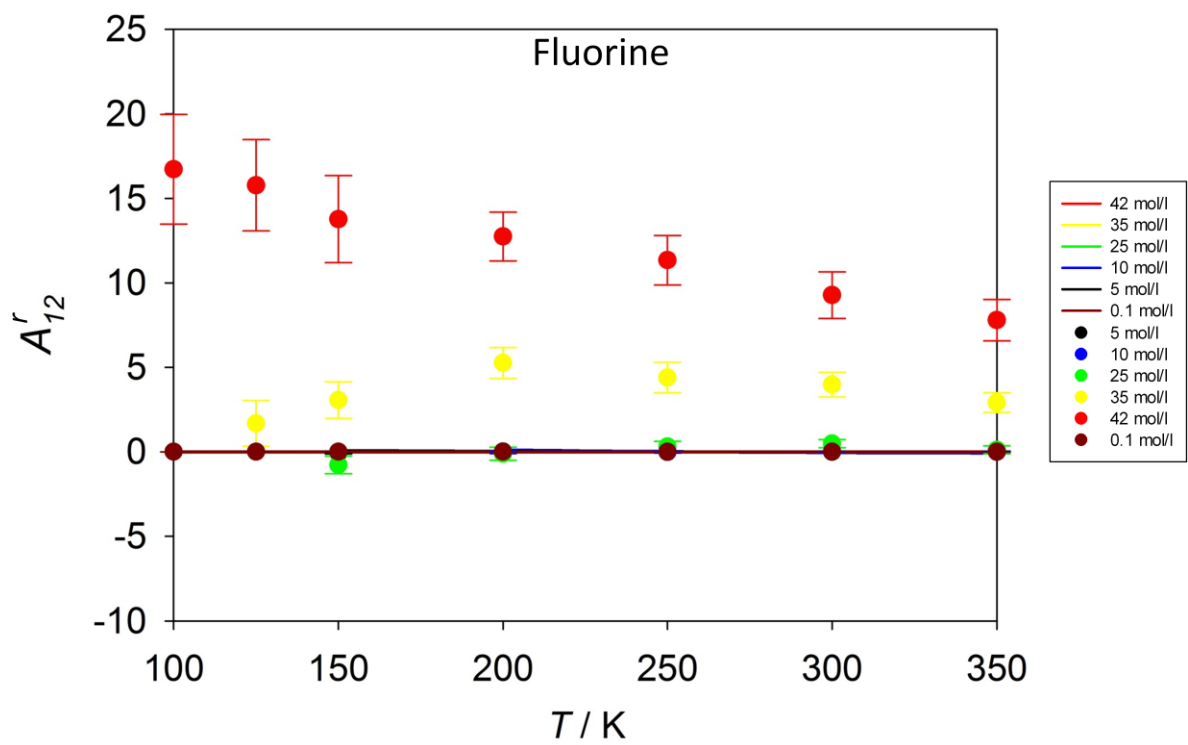
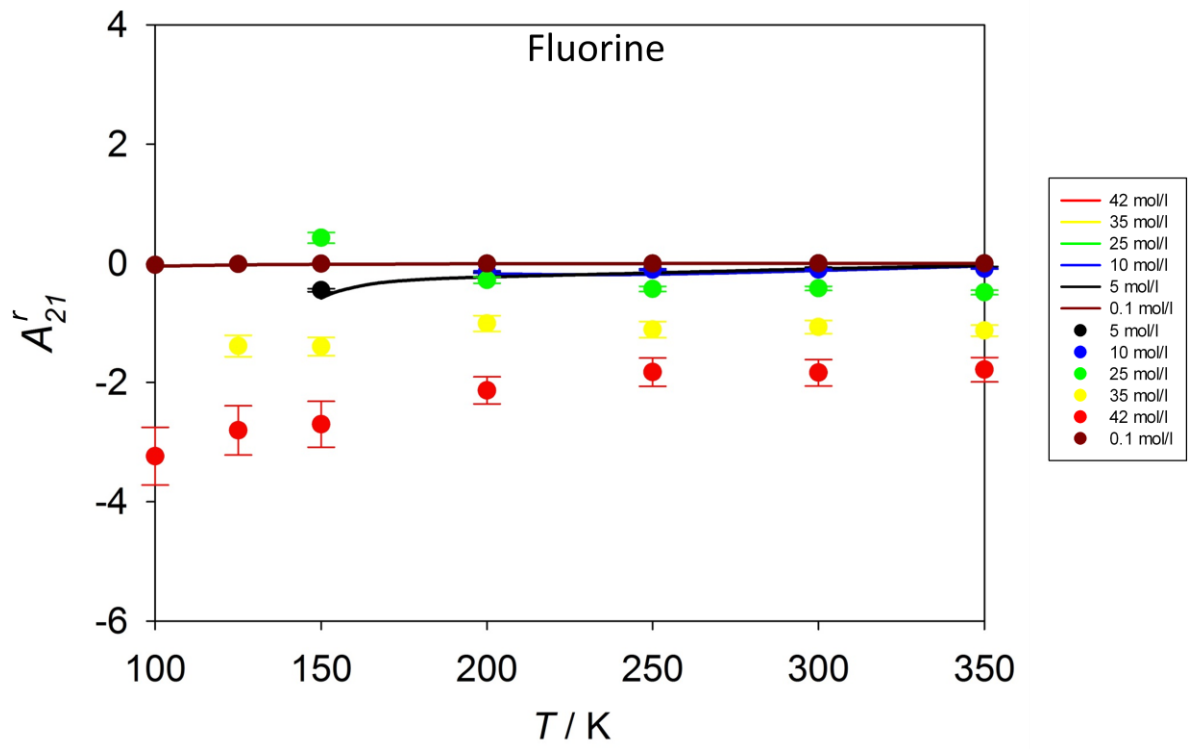
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Interaction model: J. Phys. Chem. B, 105: 12126-12133, 2001.

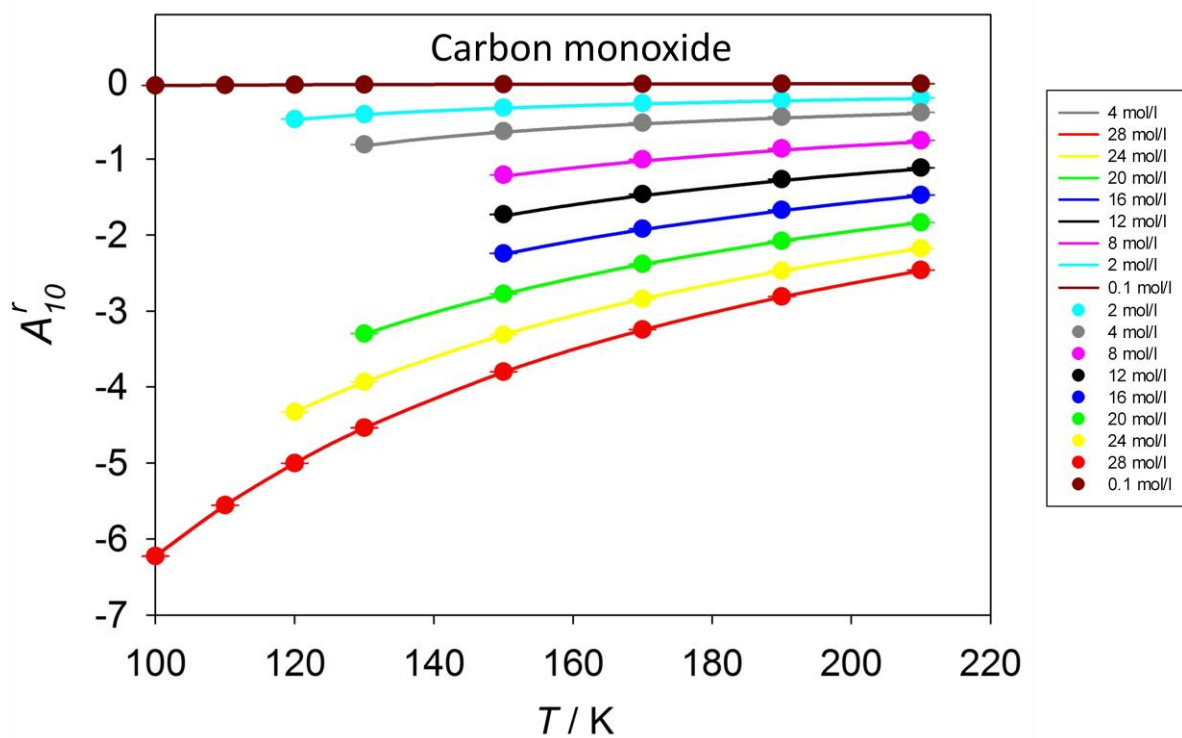
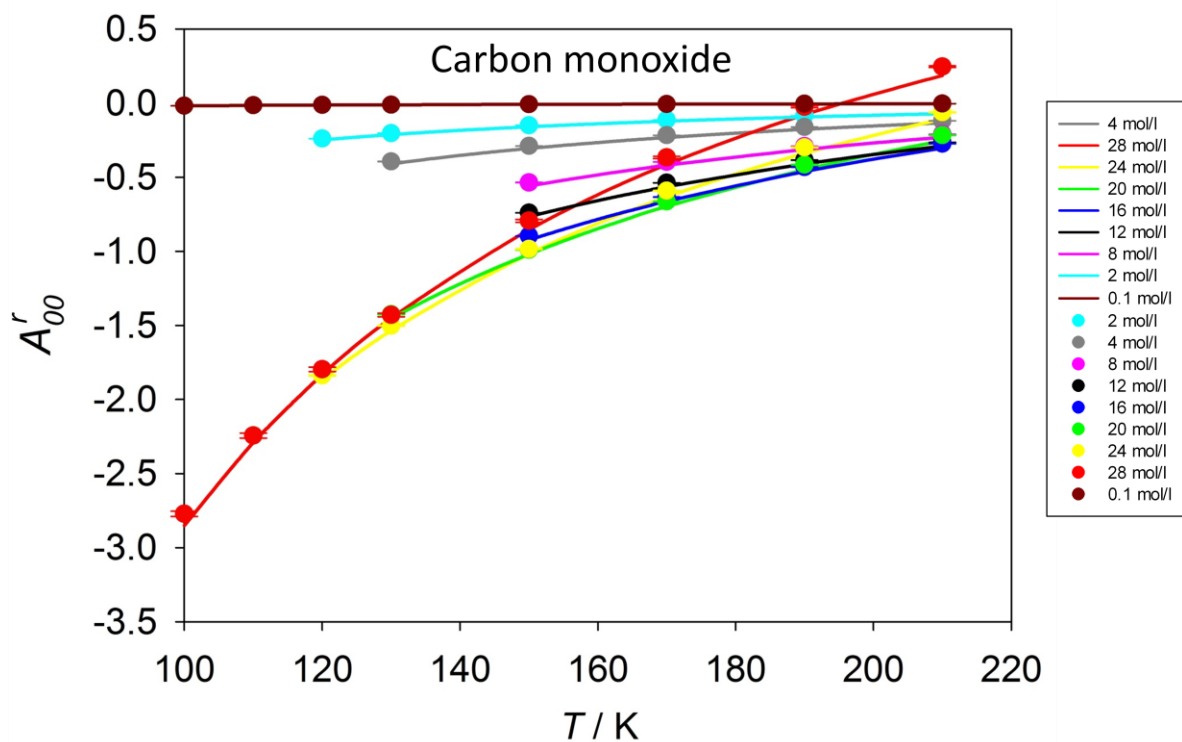


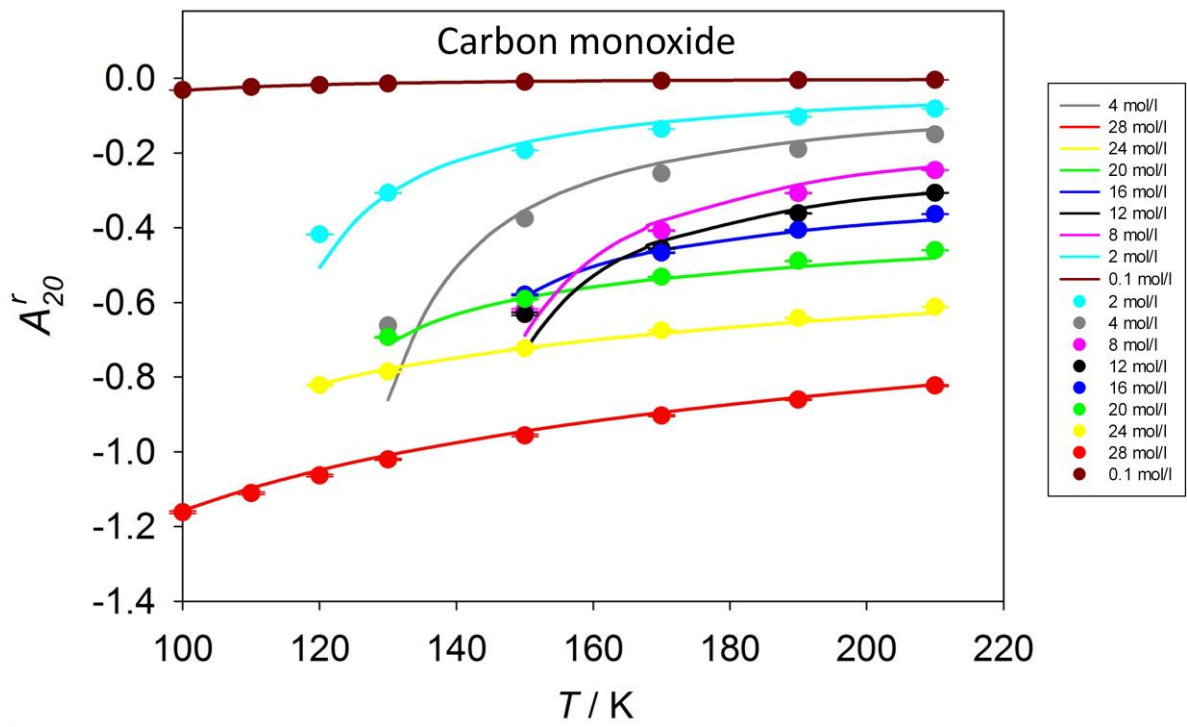
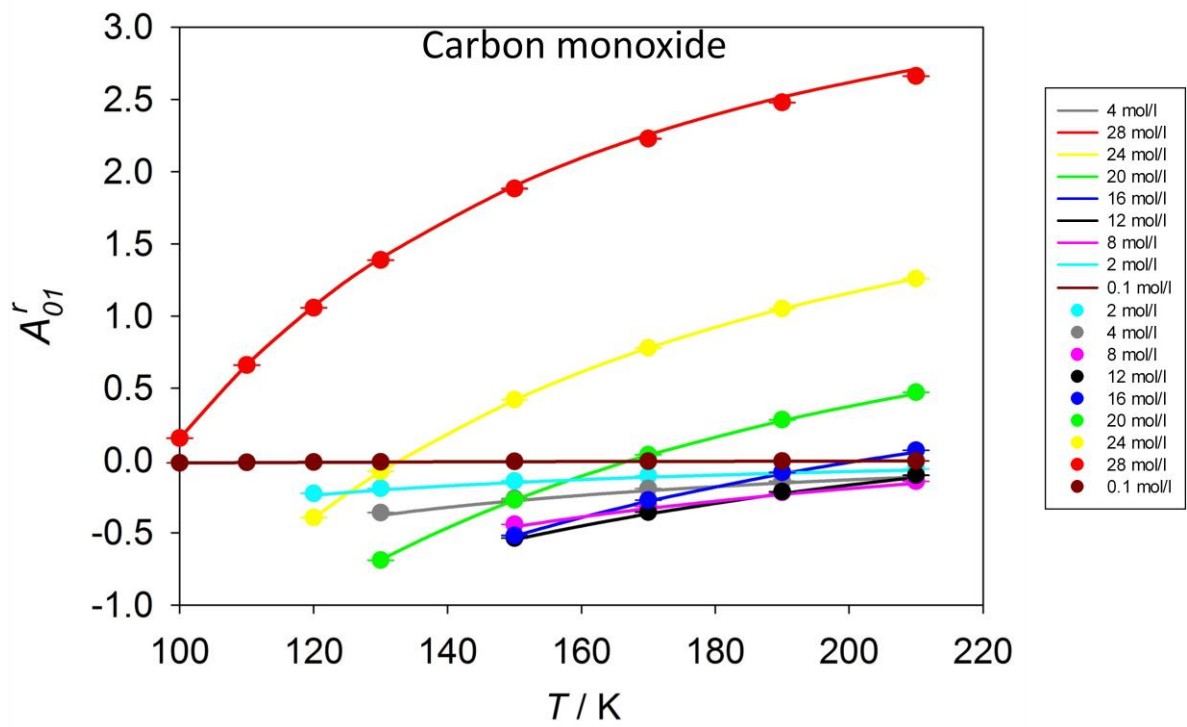


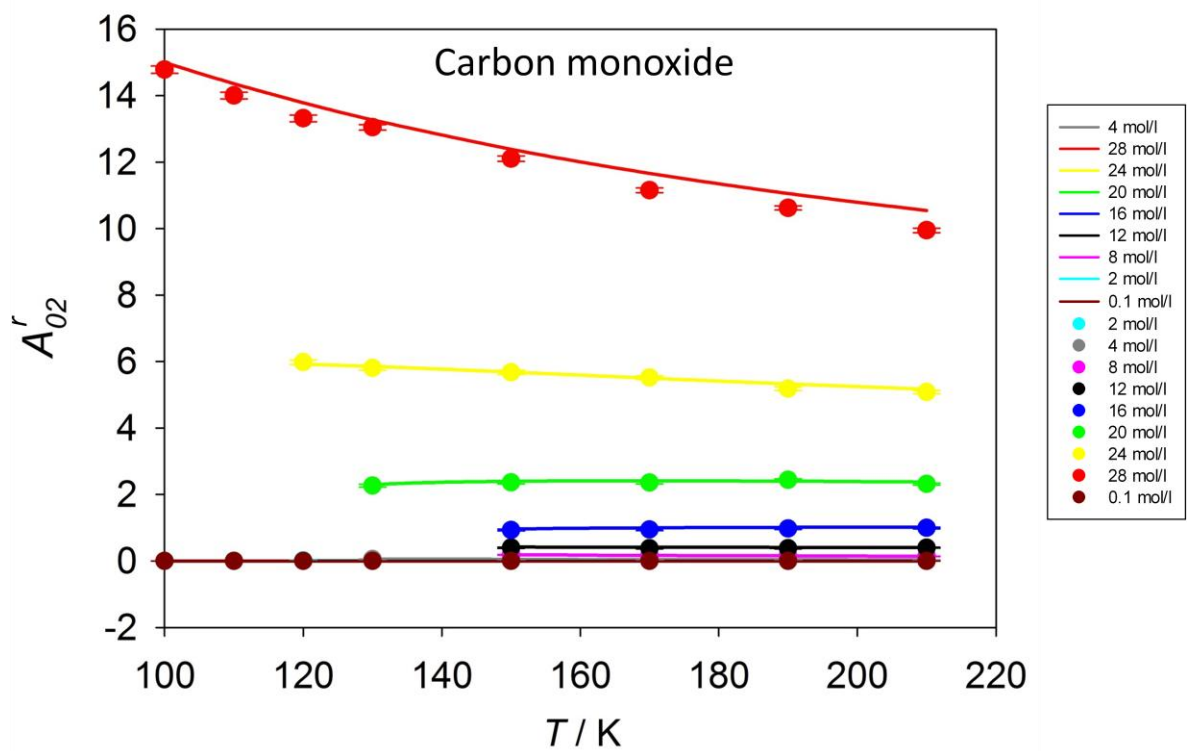
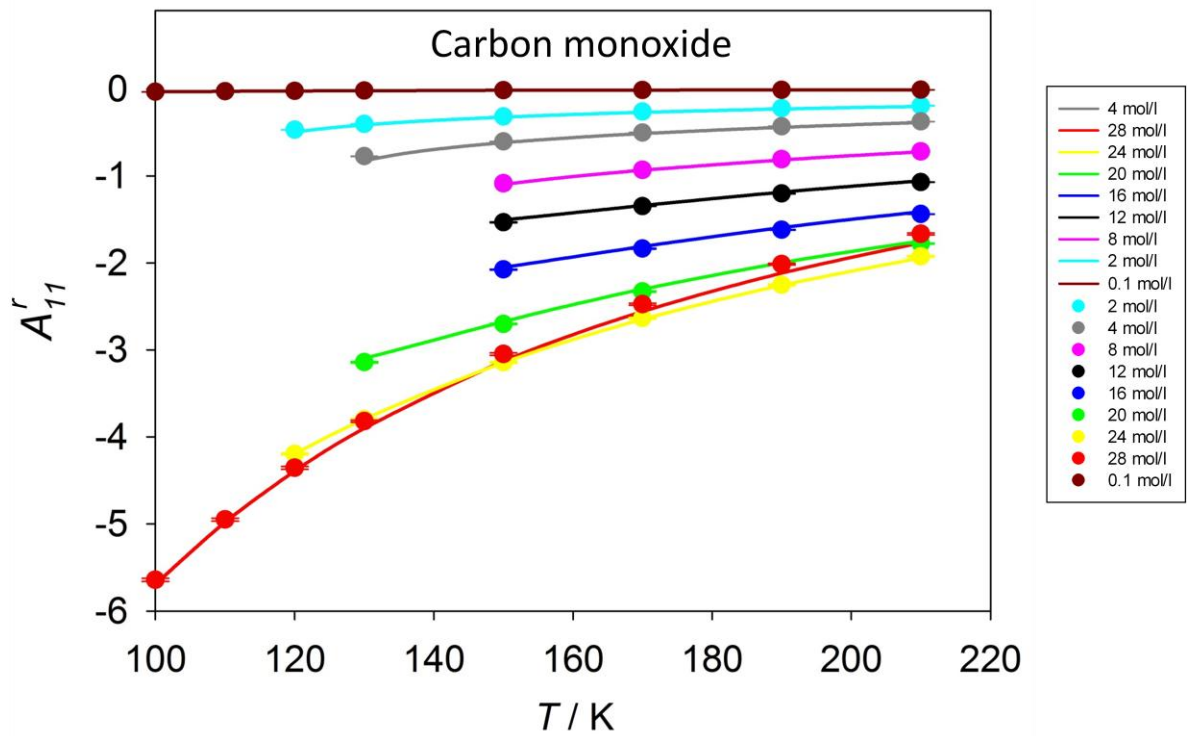


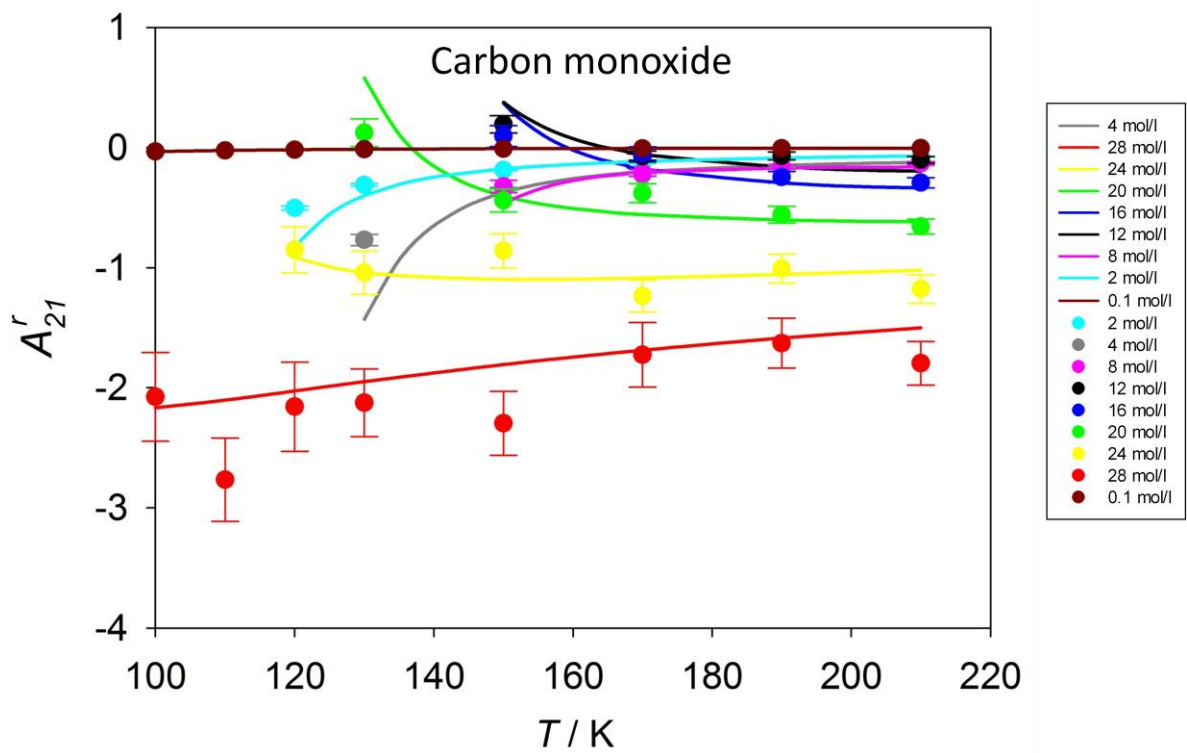
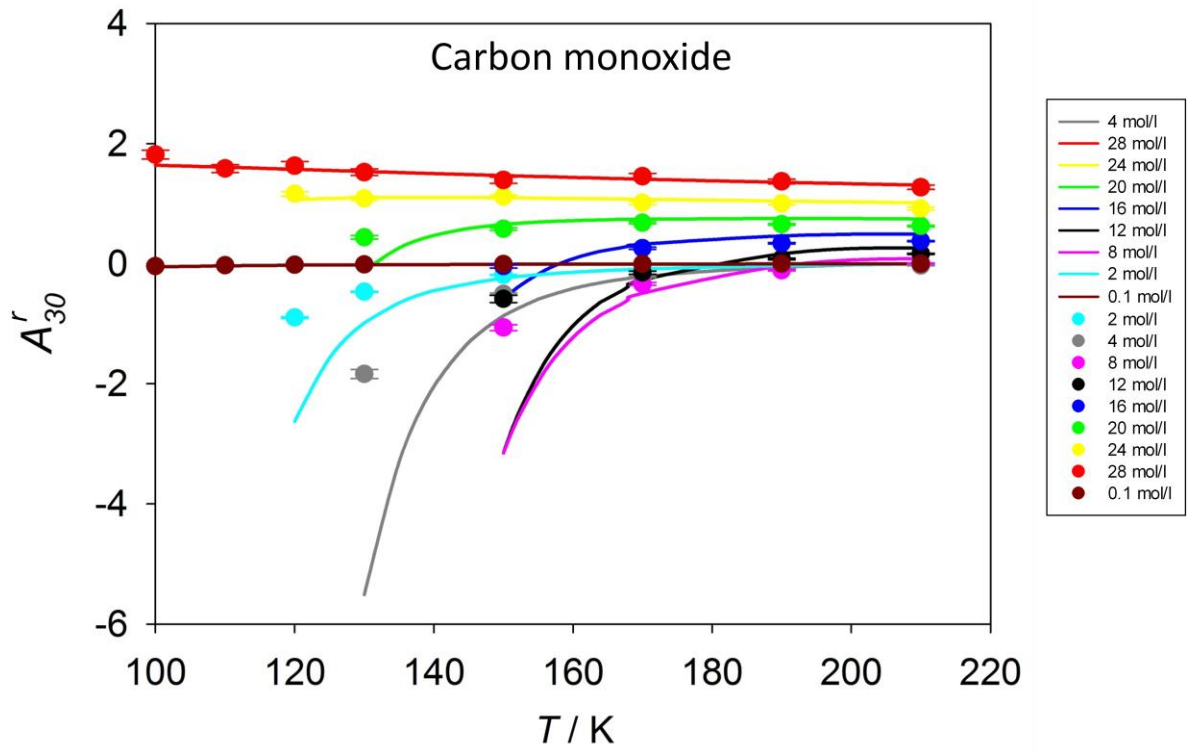


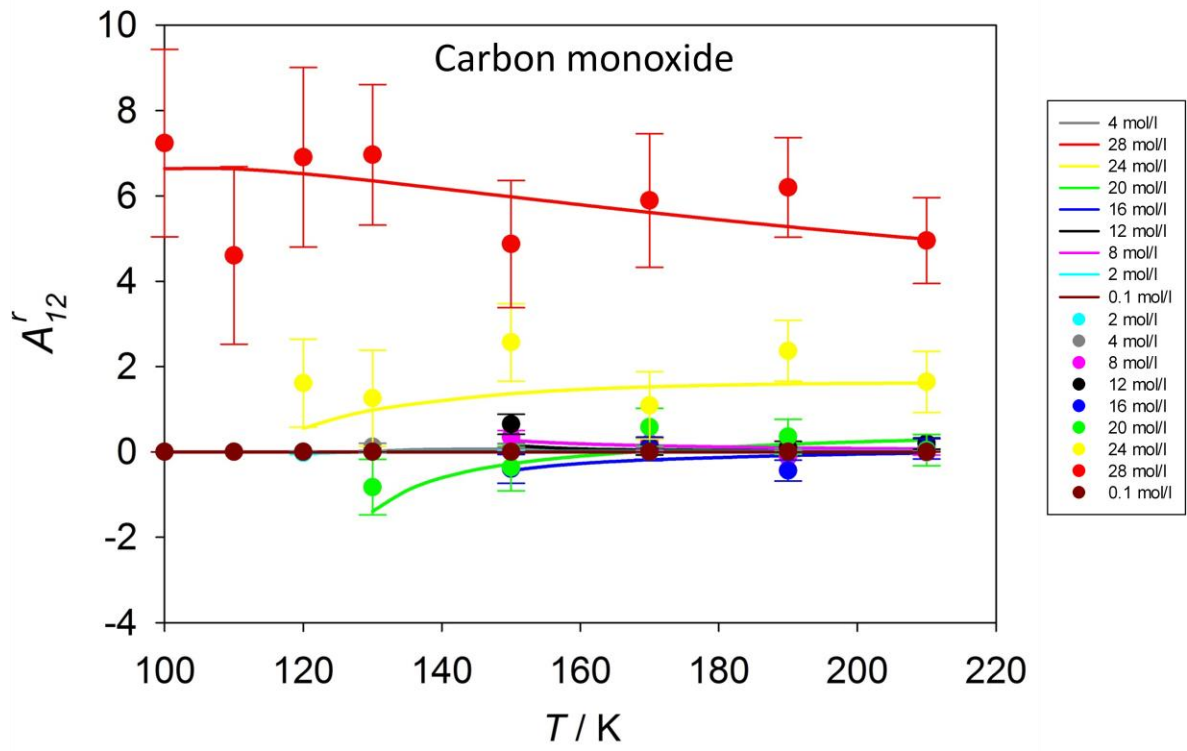
FEOS: J. Chem. Eng. Data, 51:785-850, 2006.
Interaction model: J. Chem. Phys., 119: 11396-11407, 2003.











FEOS: Int. J. Thermophys., 16(2): 519-531, 1995.
Interaction model: Fluid Phase Equilib., 315: 77-83, 2012.

