21 June 1996

ELSEVIER

Chemical Physics Letters 256 (1996) 172–178

CHEMICAL PHYSICS LETTERS

Derivation of a thermodynamic closure relation in the isothermal–isobaric ensemble using quasi-Gaussian entropy theory

M.E.F. Apol, A. Amadei, H.J.C. Berendsen

Groningen Biomolecular Sciences and Biotechnology Institute (GBB), Department of Biophysical Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Received 14 February 1996; in final form 5 April 1996

Abstract

In an analogous way as was done previously in the canonical ensemble, we derived for dilute gases an approximated thermodynamic closure relation in the isothermal–isobaric ensemble using quasi-Gaussian entropy theory. For the Gamma state, we formulated equations for the temperature dependence of various thermodynamic properties at constant pressure. The theory was applied to gaseous water and methane at 1 and 10 bar respectively, and gave for both systems an accurate prediction of the entropy and heat capacity over a large temperature interval.

1. Introduction

In recent articles [1,2] we have presented and tested quasi-Gaussian entropy theory, a theory which provides a thermodynamic closure relation for the general differential equation $(\partial S/\partial T)_V = C_V/T$. In this way it is possible to predict the temperature behavior of various thermodynamic excess properties at constant volume, based on the knowledge of a limited set of initial quantities.

The basic idea is to rewrite in the canonical ensemble expressions for the excess Helmholtz free energy and entropy in terms of the potential energy distribution function. For a macroscopic system this distribution must be uninormal and close to a Gaussian ("quasi-Gaussian"). Using a suitable framework to generate different distributions, the excess free energy is defined by the excess internal energy U^e and a limited set of its temperature derivatives, i.e. C_V^e, $(\partial C_V^e/\partial T)_V$ etc.

As the entropy is expressed in terms of T, C_V^e and further temperature derivatives, this serves as a closure relation for the general equation $(\partial S^e/\partial T)_V = C_V^e/T$, thus forming a completely defined differential equation, the *thermodynamic master equation* at constant volume. The solution of this master equation still depends on the kind of potential energy distribution function, which hence defines different "statistical states" of the system. We investigated the *Gaussian* and *Gamma state* and some approximations based on the latter, the *effective* and *confined Gamma state*.

We demonstrated that a large part of the ρT-diagram of both water and methane, except near the critical density, can be considered as a (weakly) perturbed Gamma state.

PII S0009-2614(96)00419-8

For small molecules the equations we derived provide the temperature behavior of the reduced C_V^r, S^r, U^r and A^r at constant volume (i.e. excess properties with respect to the ideal gas). In this Letter we will derive an approximation for dilute real gases which provides analogous equations in the *NpT*-ensemble for C_p^r, S^r, H^r and G^r with respect to an ideal gas at the same pressure, as the usual experimental set-up is at constant pressure, rather than at constant volume. The equations are applied to gaseous water and methane above the boiling point at 1 and 10 bar, respectively.

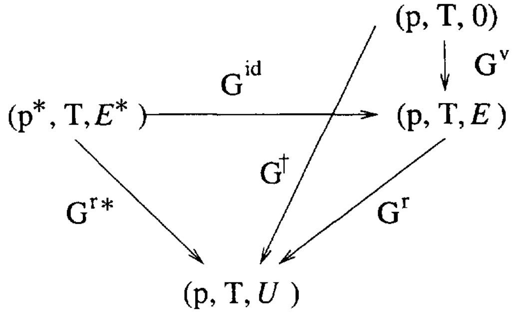

Fig. 1. Definition of the different reference systems and the thermodynamic cycle used to calculate G^r and related reduced properties.

2. Theory

Our aim is to find expressions for the excess properties with respect to a reference system with the same number of particles, temperature and pressure, but without semi-classical interactions.

In the *NpT*- or isothermal–isobaric ensemble the quasi-classical configurational partition function Δ^c (assuming as usual that we can separate the classical kinetic part of the partition function) can be written as [3,4]

$$\Delta^c(p,T,\mathscr{U}) = \int_0^\infty e^{-\beta pV}\,dV \sum \int' e^{-\beta\mathscr{U}}\,dx, \qquad (1)$$

with

$$\mathscr{U}(x) = \Phi(x) + \psi(x) + \mathscr{E}(x) \qquad (2)$$

the full potential energy of the system, including semi-classical inter and intramolecular interactions (Φ and ψ) and possible quantum bond and angle vibrations $\mathscr{E}$, and x the coordinates. (Note that $\mathscr{U}(x)$ and $\mathscr{E}$ are identical to $\nu(x)$ and E in Refs. [1] and [2]). The summation runs over all possible quantum vibration states and the prime on the integral denotes the classical angle and bond length constraints [1]. V is the volume of the system, $\beta = 1/kT$ and p the fixed pressure. We use calligraphic symbols for instantaneous quantities and the usual capitals for thermodynamic averages.

If we define a reference state with the same temperature, number of particles and pressure but without inter and intramolecular interactions and no vibrational energy (i.e. $\mathscr{U} = 0$), we see that the corresponding configurational partition function can be expressed as

$$\begin{aligned}\Delta^c(p,T,0) &= \int_0^\infty e^{-\beta pV}\,dV \sum \int' dx\\ &= \int_0^\infty e^{-\beta pV}\,dV \sum \int' e^{\beta\mathscr{U}} e^{-\beta\mathscr{U}}\,dx.\end{aligned} \qquad (3)$$

Hence, using the relation [3,4] $G = -kT \ln \Delta$, the excess free energy $G^\dagger$ is

$$\begin{aligned}G^\dagger &= -kT \ln \frac{\Delta^c(p,T,\mathscr{U})}{\Delta^c(p,T,0)}\\ &= -kT \ln \frac{\int_0^\infty e^{-\beta pV}\,dV \sum \int' e^{-\beta\mathscr{U}}\,dx}{\int_0^\infty e^{-\beta pV}\,dV \sum \int' e^{\beta\mathscr{U}} e^{-\beta\mathscr{U}}\,dx}\\ &= kT \ln\langle e^{\beta\mathscr{U}}\rangle,\end{aligned} \qquad (4)$$

where $\langle \cdots \rangle$ denotes an isothermal–isobaric ensemble average. To calculate reduced thermodynamic properties, we use the thermodynamic cycle as given in Fig. 1.

For small molecules like water and methane the semi-classical intramolecular interactions ψ are absent (or as a good approximation zero, e.g. in the case of methanol). Regarding the vibrations we can distinguish two different cases, as explained in Refs. [1] and [2].

Firstly, in the case of water, for example, the energy gap is much larger than kT in the temperature range of interest, and hence the vibrations are completely in the ground state. In that case the free energy difference between an ideal gas with and without vibrations is [1]

$$G^{\mathrm{v}} = kT\ \ln\langle \mathrm{e}^{\beta \mathcal{E}^0} \rangle_0 = \mathcal{E}_0^0, \tag{5}$$

with $\mathcal{E}_0^0$ the zero-point energy of the ideal gas (which is independent of the coordinates $\boldsymbol{x}$ and therefore from T). Hence the reduced free energy is

$$\begin{aligned} G^{\mathrm{r}} = G^{\dagger} - G^{\mathrm{v}} &= kT\ \ln\langle \mathrm{e}^{\beta(\Phi + \mathcal{E}_0 - \mathcal{E}_0^0)} \rangle \\ &= kT\ \ln\langle \mathrm{e}^{\beta \mathcal{U}^{\mathrm{r}}} \rangle \\ &= \langle \mathcal{U}^{\mathrm{r}} \rangle + kT\ \ln\langle \mathrm{e}^{\beta \Delta \mathcal{U}^{\mathrm{r}}} \rangle, \end{aligned} \tag{6}$$

with $\mathcal{U}^{\mathrm{r}} = \Phi + \mathcal{E}_0 - \mathcal{E}_0^0$ the reduced potential energy, $\Delta\mathcal{U}^{\mathrm{r}} = \mathcal{U}^{\mathrm{r}} - \langle \mathcal{U}^{\mathrm{r}} \rangle$ and $\mathcal{E}_0$ the zero-point energy of the real system, which could be dependent on $\boldsymbol{x}$.

If that real system is a dilute gas consisting of N molecules with interactions, but with an almost ideal pV term $\approx NkT$ (meaning that the average volume $\langle V \rangle$ is almost that of the ideal gas $\langle V^0 \rangle$) we have $H \approx \langle \Phi \rangle + \langle \mathcal{E}_0 \rangle + NkT$ and $H^0 = \mathcal{E}_0^0 + NkT$, where $\langle \mathcal{E}_0 \rangle$ is the average of the ground state energy over different configurations. Hence the reduced enthalpy is

$$H^{\mathrm{r}} \approx \langle \Phi \rangle + \langle \mathcal{E}_0 \rangle - \mathcal{E}_0^0 = \langle \mathcal{U}^{\mathrm{r}} \rangle = U^{\mathrm{r}}. \tag{7}$$

If, on the other hand, as in methane, higher vibrational states are accessible (because of anharmonicity [5,6]) and the vibrations are approximately independent of the semi-classical coordinates $\boldsymbol{x}$ [2], the configurational partition function can be factorized into a semi-classical and a vibrational part. Hence also the expectation value $\langle \mathrm{e}^{\beta \mathcal{U}} \rangle$ can be factorized [7]:

$$\begin{aligned} G^{\mathrm{r}} = G^{\dagger} - G^{\mathrm{v}} &= kT\ \ln\langle \mathrm{e}^{\beta \Phi} \rangle \langle \mathrm{e}^{\beta \mathcal{E}} \rangle - kT\ \ln\langle \mathrm{e}^{\beta \mathcal{E}^0} \rangle_0 \\ &= \langle \mathcal{U}^{\mathrm{r}} \rangle + kT\ \ln\langle \mathrm{e}^{\beta \Delta \mathcal{U}^{\mathrm{r}}} \rangle, \end{aligned} \tag{8}$$

with $\mathcal{U}^{\mathrm{r}} = \Phi$, and where we have used the fact that the vibrational partition function must be identical for the real system and the ideal gas, since it is independent of $\boldsymbol{x}$. In this case, considering again a dilute real gas, it follows that

$$H^{\mathrm{r}} \approx \langle \Phi \rangle = \langle \mathcal{U}^{\mathrm{r}} \rangle = U^{\mathrm{r}}. \tag{9}$$

Since in both cases the reduced free energy is linked to the variable $\mathcal{U}^{\mathrm{r}}$ with $U^{\mathrm{r}} \approx H^{\mathrm{r}}$, this can be used to form an approximated thermodynamic closure relation [1]. In both cases

$$\begin{aligned} S^{\mathrm{r}} &= -k\ \ln\langle \mathrm{e}^{\beta \Delta \mathcal{U}^{\mathrm{r}}} \rangle \\ &= -k\ \ln \int \mathrm{e}^{\beta \Delta \mathcal{U}^{\mathrm{r}}} \rho(\Delta \mathcal{U}^{\mathrm{r}})\ \mathrm{d}\Delta \mathcal{U}^{\mathrm{r}}, \end{aligned} \tag{10}$$

with $\rho(\Delta\mathcal{U}^{\mathrm{r}})\,\mathrm{d}\Delta\mathcal{U}^{\mathrm{r}}$ the probability of observing a reduced potential energy fluctuation between $\Delta\mathcal{U}^{\mathrm{r}}$ and $\Delta\mathcal{U}^{\mathrm{r}} + \mathrm{d}\Delta\mathcal{U}^{\mathrm{r}}$.

A usual macroscopic system can be considered as a collection of N identical, independent thermodynamic subsystems, the elementary systems. Each elementary system i is characterized by its reduced potential energy u_i^{r} and fluctuation $\Delta u_i^{\mathrm{r}} = u_i^{\mathrm{r}} - \langle u_i^{\mathrm{r}} \rangle$. The total reduced potential energy is given by $\mathcal{U}^{\mathrm{r}} = \sum_i^N u_i^{\mathrm{r}}$ and the total fluctuation by $\Delta\mathcal{U}^{\mathrm{r}} = \sum_i^N \Delta u_i^{\mathrm{r}}$. As the number of elementary systems N tends to infinity, applying the central limit theorem [8], it follows that the distribution $\rho(\Delta\mathcal{U}^{\mathrm{r}})$ must be uninormal and close to a Gaussian ("quasi-Gaussian"). It also must fulfil the same five physical and mathematical restrictions as formulated in Ref. [1], replacing the convergence of the excess Helmholtz free energy by the convergence of the reduced Gibbs free energy G^{r}.

Therefore, we can use the same generalized Pearson system of uninormal distributions [1,9] and the first two acceptable solutions, the Gaussian and Gamma distribution. Here we will only focus on the Gamma distribution [1,10],

$$\begin{aligned} \rho(\Delta\mathcal{U}^{\mathrm{r}}) = {} & \frac{b_1 (1/b_1^2)^{b_0/b_1^2}}{\Gamma(b_0/b_1^2)} (b_0 + b_1 \Delta\mathcal{U}^{\mathrm{r}})^{b_0/b_1^2 - 1} \\ & \times \exp\left(-\frac{b_0 + b_1 \Delta\mathcal{U}^{\mathrm{r}}}{b_1^2} \right), \end{aligned} \tag{11}$$

where the parameters b_0 and b_1 are linked to the central moments $M_k = \langle (\Delta\mathcal{U}^{\mathrm{r}})^k \rangle$ of the reduced potential energy $\mathcal{U}^{\mathrm{r}}$ as [1] $b_0 = M_2$ and $b_1 = M_3/2M_2$.

---

[1] Note that an exact thermodynamic closure relation can only be obtained using a reference system with no potential energy and zero pressure, since the free energy with respect to this reference is given by $G' = \langle \exp\{\beta\mathcal{H}\} \rangle$, where $\mathcal{H} = \mathcal{U} + pV$. The moments of $\mathcal{H}$ are exactly related to the ideal reduced C_p' and further temperature derivatives. Unfortunately, the free energy of this reference is infinite, and hence the reference as such is useless.

We already obtained $U^{\mathrm{r}} \approx H^{\mathrm{r}}$. We further assume that for the Gamma state the central moments of $\mathcal{U}^{\mathrm{r}}$ up to the third one are (numerically) identical to those of $\mathcal{H}^{\mathrm{r}} = \mathcal{U}^{\mathrm{r}} + p(V - V^0)$, i.e. $\langle V^k \rangle \approx \langle V^{0k} \rangle$ for $k = 1 \ldots 3$ and $\langle \Delta\mathcal{U}^{\mathrm{r}} \Delta V \rangle \approx 0$.

From elementary statistical mechanics [3,4] it is known that the total isobaric heat capacity is proportional to the second moment of the instantaneous enthalpy. Hence it is easy to show that

$$M_2 = \langle (\Delta\mathcal{U}^{\mathrm{r}})^2 \rangle \approx \langle (\Delta\mathcal{H}^{\mathrm{r}})^2 \rangle = kT^2 C_p^{\mathrm{r}}, \tag{12}$$

with C_p^{r} the reduced heat capacity. In a similar way as in Ref. [1], we can derive that

$$M_3 = \langle (\Delta\mathcal{U}^{\mathrm{r}})^3 \rangle \approx \langle (\Delta\mathcal{H}^{\mathrm{r}})^3 \rangle = (kT)^2 \left\{ 2TC_p^{\mathrm{r}} + T^2 \left(\frac{\partial C_p^{\mathrm{r}}}{\partial T} \right)_p \right\}. \tag{13}$$

Solving the integral in Eq. (10) with Eqs. (11), (12) and (13) and the relations for b_0 and b_1 we obtain (see also Ref. [1])

$$S^{\mathrm{r}} = C_p^{\mathrm{r}} \left\{ \frac{1}{\theta} + \frac{1}{\theta^2} \ln(1 - \theta) \right\}, \tag{14}$$

with

$$\theta = 1 + \frac{T\left(\partial C_p^{\mathrm{r}}/\partial T\right)_p}{2C_p^{\mathrm{r}}}. \tag{15}$$

In an analogous way as in the canonical ensemble we can define an *intrinsic entropy function* [1,2] ω, a dimensionless and intensive property, as

$$\omega = \frac{S^{\mathrm{r}}}{C_p^{\mathrm{r}}}, \tag{16}$$

being a kind of "resistance" of the system against increasing the order by lowering the temperature. Combining this with the general thermodynamic relation $(\partial S/\partial T)_p = C_p/T$, we obtain

$$\frac{C_p^{\mathrm{r}}}{T} = \omega \left(\frac{\partial C_p^{\mathrm{r}}}{\partial T} \right)_p + C_p^{\mathrm{r}} \left(\frac{\partial \omega}{\partial T} \right)_p, \tag{17}$$

the *thermodynamic master equation* at constant pressure. For the Gamma distribution (Eqs. (14) and (15)) the solution of this master equation is mathematically identical to the one at constant volume [1,2]:

$$\theta(T) = \frac{T_0 \theta_0}{T(1 - \theta_0) + T_0 \theta_0}, \tag{18}$$

$$C_p^{\mathrm{r}}(T) = C_{p0}^{\mathrm{r}} \left(\frac{\theta(T)}{\theta_0} \right)^2, \tag{19}$$

$$S^{\mathrm{r}}(T) = C_p^{\mathrm{r}}(T) \left\{ \frac{1}{\theta(T)} + \frac{1}{\theta^2(T)} \ln[1 - \theta(T)] \right\}, \tag{20}$$

$$H^{\mathrm{r}}(T) = H_0^{\mathrm{r}} + (T - T_0) C_{p0}^{\mathrm{r}} \frac{\theta(T)}{\theta_0} \tag{21}$$

and

$$G^{\mathrm{r}}(T) = H_0^{\mathrm{r}} - \frac{T_0 C_{p0}^{\mathrm{r}}}{\theta_0} - \frac{T C_{p0}^{\mathrm{r}}}{\theta_0^2} \times \ln \left(\frac{T(1 - \theta_0)}{T_0} \frac{\theta(T)}{\theta_0} \right), \tag{22}$$

where C_{p0}^{r}, H_0^{r} and θ_0 are the values of C_p^{r}, H^{r} and θ at the arbitrary reference temperature T_0, and θ is given by Eq. (15). In Refs. [1] and [2] we decribed the properties of a left-skewed or right-skewed Gamma distribution, defining the Γ^- and Γ^+ state. From these properties it follows that θ tends to one, and both $C_p^{\mathrm{r}}(T)$ and $S^{\mathrm{r}}(T)$ tend to zero if $T \to \infty$, with C_p^{r} always positive and S^{r} always negative, hence $\omega < 0$. Moreover, the value $\omega = -\frac{1}{2}$ denotes a perfectly symmetric enthalpy distribution (compatible with a Gaussian state). For a Γ^- state (which must be regarded only as an approximation to a more complex physical statistical state) $-\frac{1}{2} < \omega < 0$, while for a Γ^+ state $\omega < -\frac{1}{2}$.

Solutions of the generalized Pearson system of distributions beyond the Gamma distribution are mathematically much less manageable. Therefore, we will only focus on the exact Gamma solution and an approximation, the *effective Gamma state* [1,2], in which the parameter θ_0 is calculated from $\omega_0 = S_0^{\mathrm{r}}/C_{p0}^{\mathrm{r}} = 1/\theta_0 + (1/\theta_0^2) \ln(1 - \theta_0)$, rather than using Eq. (15). In this way, especially the entropy can be predicted efficiently [1,2].

To calculate experimental reduced properties X^{r}, we must again use the thermodynamic cycle as given in Fig. 1, where for a pressure $p^* \approx 0$ (ideal gas condition) we have $X^{r*} = X(p) - X(p^*)$. Observing further that the free energy difference between the two ideal gas states $G^{id} = \int_{p^*}^{p} V\,dp = kT\ln(p/p^*)$ and $S^{id} = -Nk\ln(p/p^*)$ since $H^{id} = 0$ for an ideal gas, we see that

$$H^r = H(p,T) - H(p^*,T), \tag{23}$$

$$S^r = S(p,T) - S(p^*,T) + Nk\ln\frac{p}{p^*} \tag{24}$$

and

$$C_p^r = C_p(p,T) - C_p(p^*,T) = T\left(\frac{\partial S^r}{\partial T}\right)_p. \tag{25}$$

3. Results

Experimental data for methane were obtained from Angus et al. [11] and for water from Schmidt [12]. Values of C_p^r were obtained directly from the tables in the case of methane, and were calculated numerically from the reduced entropy data in the case of water using Eq. (25).

For methane the results of C_p^r and S^r at a pressure $p = 10$ bar, using $p^* = 0.25$ bar, are given in Fig. 2. For a reference temperature $T_0 = 155$ K, we see an excellent agreement between the experimental values and the predictions from the theory over a temperature range of more than 450 K. In this case the effective and the exact θ_0 are identical, which means that the statistical state is virtually an exact Gamma state. Choosing the reference temperature at 400 K, we basically obtain the same results over the whole temperature range. It must be noted that at high temperature the relative errors in C_p^r and S^r are quite large, and hence the definition of the Gamma state (especially the Γ^- states, see Ref. [2]) is in general not sufficiently accurate to predict values at temperatures much lower than T_0.

For water the results of C_p^r and S^r at a pressure $p = 1.0$ bar, using $p^* = 0.01$ bar, are given in Fig. 3. For $T_0 = 533$ K, from ~ 450 to 1000 K the agreement with the experimental data is good. Below 450 K there is some deviation, because of the stronger non-ideality, in water, due to the long-range electrostatic interactions. The small deviations above ~ 800 K are artefacts of the numerical calculation of experimental C_p^r values. Using $T_0 = 713$ K, we obtain

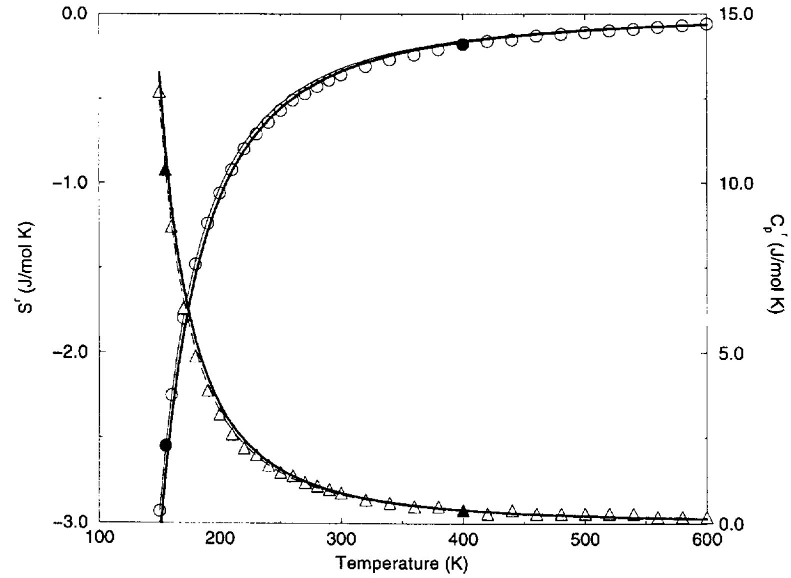

Fig. 2. Experimental results and effective Gamma predictions of S^r and C_p^r for methane at $p = 10$ bar. Legend: S^r experimental (○) and predictions for low (———) and high T_0 (———), C_p^r experimental (△) and predictions for low (-----) and high T_0 (▬▬▬). The values at the reference temperatures T_0 are denoted by solid symbols.

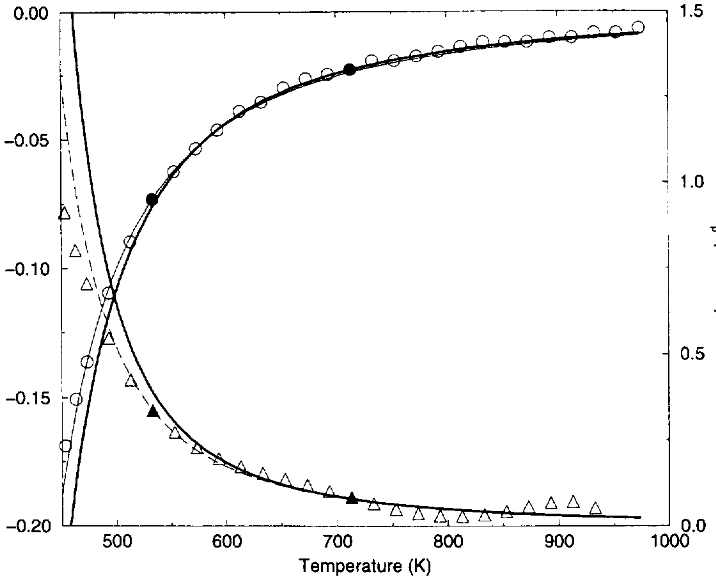

Fig. 3. Experimental results and effective Gamma predictions of S^r and C_p^r for water at $p = 1$ bar. Legend: S^r experimental (○) and predictions for low (———) and high T_0 (———), C_p^r experimental (△) and predictions for low (-----) and high T_0 (▬▬▬▬▬). The values at the reference temperatures T_0 are denoted by solid symbols.

virtually identical results, except for the temperature range below ~ 550 K, due to the larger relative errors in the input data, as discussed before.

4. Discussion and conclusions

In this Letter we have demonstrated that for dilute real gases also at constant pressure it is possible to derive a thermodynamic closure relation, albeit an approximated one. Clearly, because of the nature of the approximation, this approach will not be applicable to dense gases or liquids. The equations for the temperature dependence of various thermodynamic properties were tested for water and methane. For both gases the theory gives good results in a temperature interval of more than 450 K. One could expect that the method is applicable for methane, or in general apolar molecules, at even larger pressures.

Acknowledgement

We would like to thank Dr. J. Mavri (National Institute of Chemistry, Slovenia) and Professor A. Di Nola (Rome) for carefully reading the manuscript and stimulating discussions. This work was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO) and by the Training and Mobility of Researchers (TMR) Program of the European Community.

References

[1] A. Amadei, M.E.F. Apol, A. Di Nola and H.J.C. Berendsen, J. Chem. Phys. 104 (1996) 1560.
[2] M.E.F. Apol, A. Amadei and H.J.C. Berendsen, J. Chem. Phys., in press.
[3] D.A. McQuarrie, Statistical mechanics (Harper and Row, New York, 1976).
[4] J.P. Hansen and I.R. McDonald, Theory of simple liquids, 2nd Ed. (Academic Press, London, 1986).
[5] L.H. Jones and R.S. McDowell, J. Mol. Spectry. 3 (1959) 632.
[6] R.S. McDowell and F.H. Kruse, J. Chem. Eng. Data 8 (1963) 547.
[7] N.I. Johnson and S. Kotz, Discrete distributions (Houghton Mifflin, New York, 1969).
[8] H. Cramér, Mathematical methods of statistics (Princeton Univ. Press, Princeton, 1946).

[9] J.K. Ord, Families of frequency distributions Vol. 20. Handbook of statistical distributions (Griffin, London, 1972).
[10] J.K. Patel, C.H. Kapadia and D.B. Owen, volume 20 of Statistics: textbooks and monographs (Marcel Dekker, New York, 1976).
[11] S. Angus, B. Armstrong and K.M. de Reuck, national thermodynamic tables of the fluid state, vol. 5. Methane (Pergamon Press, Oxford, 1976).
[12] E. Schmidt, Properties of water and steam in SI-units (Springer, Berlin, 1969).