

Thermodynamic properties of air at high temperature

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Thermodynamic properties of air are obtained for air at high temperature using the partition function approach in statistical mechanics. The composition of air is simplified to be made up of seven species namely N_2 , O_2 , NO , NO^+ , N , O and e^- . Curve fits are obtained for the specific heat capacity of air at temperatures ranging upto 30000K and pressures varying from 1atm to 90atm.

Nomenclature

Q	Partition function
Q_{tr}	Translational partition function
Q_{int}	Internal partition function
m	Mass, Kg
k	Boltzmann constant, SI
h	Planck's constant, SI
E_{vib}	Vibrational energy
E_{rot}	Rotational energy
$\omega_e, \omega_e x_e, \omega_e y_e$	Spectroscopic constants - anharmonic oscillator
c	Speed of light
D_0	Dissociation energy referenced to first energy level
D_e	Dissociation energy
B_ν, D_ν	Spectroscopic constants - non-rigid rotator
α_e, β_e	Spectroscopic constants - corrections to rotator
r_e	Equilibrium distance
C_p	Specific heat capacity
K_p	Equilibrium constant of pressure
p_i	Partial pressure of the i th species
X_i	Mole fraction of the i th species
T	Temperature
<i>Subscript</i>	
i	Variable to denote species

I. Introduction

Thermodynamic properties of gaseous mixtures are of interest in both the aerospace and the astrophysics community. It has applications in modelling and analysis of re-entry vehicles. Apart from this, it is necessary to understand and model stellar phenomena among many other interests.

A. Methodology

The partition function approach commonly used in statistical mechanics is employed in the calculation of thermodynamic properties. The gradients of the partition function provide the necessary thermodynamic parameters. For mixtures, the thermodynamic properties turn out to be weighted sum of the properties of

individual components. The composition of each of the components mentioned previously were computed for a range of temperatures and pressures. Using this data, specific heat for air was computed. An algorithm for employed to calculate the curve fits for the generated specific heat for air.

II. Model

A. Partition function

The partition function can be factorised as the product of the translational $Q_{tr,i}$ and the internal $Q_{int,i}$ contributions as:

$$Q_i = Q_{tr,i} \times Q_{int,i} \quad (1)$$

$$Q_{tr,i} = \left(\frac{2\pi m_i kT}{h^2} \right)^{\frac{3}{2}} \quad (2)$$

The internal partition function has to be calculated differently depending on the type of molecules. The methodology is discussed below.

1. Diatomic molecules

The energy of a diatomic molecule can be split into its respective components namely electronic and rotational energy.

$$E_{nJv} = E_{el}(n) + E_{vib}(n, v) + E_{rot}(n, v, J) \quad (3)$$

The vibrational energy associated with the ν^{th} vibrational level of the n^{th} electronic state of a diatomic molecule is expressed in analytical form as :

$$\frac{E_{vib}(n, v)}{hc} = \omega_e \left(\nu + \frac{1}{2} \right) - \omega_e x_e \left(\nu + \frac{1}{2} \right)^2 + \omega_e y_e \left(\nu + \frac{1}{2} \right)^3 + \omega_e z_e \left(\nu + \frac{1}{2} \right)^4 \quad (4)$$

The above expression can be rewritten with the energy referenced to the first vibrational level. After substituting the expression becomes:

$$\frac{E_{vib}(n, v)}{hc} = \frac{E_{vib}(n, 0)}{hc} + \omega_0 \nu - \omega_0 x_0 \nu^2 + \omega_0 y_0 \nu^3 + \omega_0 z_0 \nu^4 \quad (5)$$

where,

$$\omega_0 = \omega_e - \omega_e x_e + \frac{3}{4} \omega_e y_e + \frac{1}{8} \omega_e z_e$$

$$\omega_0 x_0 = \omega_e x_e - \frac{3}{2} \omega_e y_e - \frac{3}{2} \omega_e z_e$$

$$\omega_0 y_0 = \omega_e y_e + 2 \omega_e z_e$$

$$\omega_0 z_0 = \omega_e z_e$$

Assuming equation 5 is valid for all vibrational states up to dissociation, we can determine the maximum permissible value ν_{max} of the vibrational quantum number of each rotationless ($J = 0$) molecular state from the equation:

$$\omega_0 \nu_{max} - \omega_0 x_0 \nu_{max}^2 + \omega_0 y_0 \nu_{max}^3 + \omega_0 z_0 \nu_{max}^4 = D_0(n) \quad (6)$$

The rotational energy of a non-rigid rotator associated with the ν_{th} vibrational level of the n_{th} electronic state reads:

$$\frac{E_{vib}(n, v, J)}{hc} = B_v J(J+1) - D_v J^2(J+1)^2 \quad (7)$$

where,

$$\frac{E_{vib}(n, v, J)}{hc} = B_v J(J+1) - D_v J^2(J+1)^2 \quad (8)$$

$$B_v = B_e - \alpha_e(\nu + \frac{1}{2}) \quad (9)$$

$$D_v = D_e - \beta_e(\nu + \frac{1}{2}) \quad (10)$$

The maximum permissible value J_{max} of the rotational quantum number for each vibrational quantum number is determined comparing the vibrational-rotational energy with the dissociation energy relative to the electronic we are considering .For a diatomic molecule the potential curve is given by :

$$U_0 = D_e(1 - e^{-\beta(r-r_e)})^2 \quad (11)$$

where β is given by the equation

$$\beta = \sqrt{\frac{2\pi^2 c \mu}{D_e h}} w_e \quad (12)$$

When we consider a rotating molecule on the basis of classical mechanics, we must introduce an additional term in eq.(11) : a centrifugal potential. Thus, when the angular momentum is J , effective potential energy (in cm^{-1}) becomes :

$$U_J(r) = U_0 + \frac{h}{8\pi^2 c \mu r^2} J(J+1) \quad (13)$$

A series of potential curves for consecutive J 's can be constructed. These potential curves show a maximum at a larger distance respect to the equilibrium distance for $0 \leq J \leq J_{max}$. For $J = 0$ no centrifugal distortion occurs and there is some maximum value of J beyond which the potential curve no longer displays a minimum. This implies that for $J = 0$ all vibrational states with energy lower than the dissociation limit are present; while there are no stable states with J larger than J_{max} . The centrifugal distortion of the potential energy determines the existence of "quasi-bound" states above the dissociation limit for each vibrational state. In order to calculate the number of rotational states above the dissociation limit for each vibrational state, we differentiate eq.(13) with respect to r , setting this derivative equal to zero and solving the resulting equation for the value of r at the hump (called r_m) as a function of J for any electronic state of the molecule.

$$\frac{\partial U}{\partial r} = 2D_e\beta(e^{-\beta(r-r_e)} - e^{-2\beta(r-r_e)}) - \frac{2}{r^3} \frac{h}{8\pi^2 c \mu} J(J+1) = 0 \quad (14)$$

Then the value of the potential at r_m is calculated for each J . This potential is compared with energy as calculated from the coupled vibrational-rotational energy expression for any assumed ν and J is varied until these two energy values are equal . When this point is reached, one has a compatible ν, J combination.

$$E_m = \frac{E_{vib}(n, 0)}{hc} + \omega_0 \nu - \omega_0 x_0 \nu^2 + \omega_0 y_0 \nu^3 + \omega_0 z_0 \nu^4 + B_v J(J+1) - D_v J^2(J+1)^2 \quad (15)$$

$$U_J(r_m) = D_e\beta(1 - e^{-\beta(r-r_e)})^2 - \frac{h}{8\pi^2 c \mu r_m^3} J(J+1) \quad (16)$$

Once the maximum number of vibrational levels for each electronic state and the maximum number of rotational states for each vibrational have been determined, the internal partition function can be calculated by the following expression.

$$Q_{int} = \frac{1}{\sigma} \sum_n^{n_{max}} g_n e^{\frac{-E_e(n)}{kT}} \sum_{\nu}^{\nu_{max}(n)} e^{\frac{-E_{vib}(n, \nu)}{kT}} \sum_J^{J_{max}(n, \nu)} e^{\frac{-E_{rot}(n, \nu, J)}{kT}} \quad (17)$$

For the coupled vibrational and rotational energies of the molecule, Mayer and Mayer⁵ have approximated the summation for internal partition function and arrived at the following expression for the molecular internal partition function of a symmetric diatomic gas:

$$Q_{int} = \frac{1}{\sigma} \sum_n^{n_{max}} g_n e^{\left[-\frac{E_{el}(n)}{kT}\right]} \left[\frac{1}{\sigma(1-e^{-u})} \left(1 + \frac{\sigma}{3} + \frac{\sigma^2}{15} + \frac{8\gamma^2}{15} - \frac{\delta}{1-e^{-u}} + \frac{2x_e U}{(1-e^{-u})^2} \right) \right] \quad (18)$$

where

$$\delta = \frac{\alpha_e}{B_e} \quad (19)$$

$$\sigma = \left(1 - \frac{1}{2}\delta_e\right) B_e h c / k T \quad (20)$$

$$u = (1 - 2x_e) \omega_e h c / k T \quad (21)$$

$$\gamma = B_e / w_e \quad (22)$$

The above terms differ with each electronic level and thus these values have to be separately evaluated for each electronic level.

2. Polyatomic molecules

The internal partition function of polyatomic molecules by analogy with diatomic molecules can be written in the general case in the following way:

$$Q_{int} = \frac{1}{\sigma} \sum_i p_i e^{-\frac{h c}{k T} T_0^i} \sum_{\nu_1} \sum_{\nu_2} \sum_{\nu_m} p_{\nu} e^{-\frac{h c}{k T} G_0^i(\nu_1, \nu_2, \dots, \nu_m)} \sum_J \sum_{k=-J}^{k=J} (2J+1) e^{-F_{\nu}^i(J,k)} \quad (23)$$

Increasing temperature, the use of the method of direct summation becomes impossible both because of the absence of data for the high vibrational-rotational energy levels including the ground electronic state of almost all polyatomic molecules, as well as the absence of sufficiently accurate knowledge of the dependence of the energy of these levels on the quantum numbers ν_n and J . Then calculations of the thermodynamic functions of polyatomic molecules still use the "rigid rotator harmonic oscillator" approximation. Deviations from this model, the presence of excited electronic states and other effects are taken into account in the form of corrections. This approximation assumes the vibrations of the molecule in its electronic ground state as harmonic, then the upper limits for ν_n and J in the partition function and its derivatives approach infinity. Then, the internal partition function for the molecule in the electronic ground state is given by:

$$Q_{int} = p X Q_{rr,-h,0}^{(X)} = p X Q_{rr}^{(X)} X Q_{h,o}^{(X)} \quad (24)$$

where,

$$Q_{h,0} = \prod_{n=1}^m \left[1 - e^{-\frac{h c}{k T} \nu_n} \right]^{-d_n} \quad (25)$$

$$Q_{r,r} = \frac{k T}{\sigma h c B_0} \quad (26)$$

for linear molecules and,

$$Q_{r,r} = \sqrt{\frac{\pi}{A_0 B_0 C_0} \left(\frac{k T}{h c} \right)^3} \quad (27)$$

where, the quantities A_0 , B_0 and C_0 are the rotational constants related to the principal moments of inertia of the molecule.

$$A_0 = \frac{h}{8\pi^2 c I_A}, B_0 = \frac{h}{8\pi^2 c I_B}, C_0 = \frac{h}{8\pi^2 c I_C} \quad (28)$$

B. Thermodynamic properties

All the thermodynamic properties of a gas can be obtained from its partition function. In this report, only the method to calculate the specific heat of a gas is discussed. The specific heat of a mixture is the mass fraction weighted sum of the specific heats of the individual gases. Hence it becomes necessary to calculate the composition of the mixture at various temperatures.

Given below is the equation to find the C_p of a simple gas:

$$C_{p,int} = R \left[2T \left(\frac{\partial \ln Q_{int}}{\partial T} \right)_V + T^2 \left(\frac{\partial^2 \ln Q_{int}}{\partial T^2} \right)_V \right] \quad (29)$$

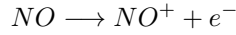
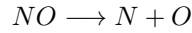
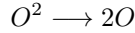
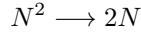
$$C_p = C_{p,int} + \frac{5}{2}R \quad (30)$$

C. Composition of the mixture

As discussed in the previous subsection, it is necessary to compute the equilibrium concentrations of the various gases that may be present in the mixture. This requires a list of all the reactions which undergo with the given set of species. In this present study, only seven species namely N_2 , O_2 , NO , NO^+ , N , O and e^- are considered.⁴ The respective equations are:



Initially, it is considered that the atmosphere has a composition of 79% of Nitrogen and 21% of Oxygen. Additional equations are required for calculation of individual species concentrations. These are:



The molar concentration is proportional to the partial pressure of the gas. Hence it is possible to express molar concentrations in terms of its partial pressure.

To solve for the composition of each of the components, we can by species conservation get two equations:

$$2p_{N^2}^r = 2p_{N^2}^p + p_{NO}^p + p_N^p + p_{NO^+}^p \quad (31)$$

$$2p_{O^2}^r = 2p_{O^2}^p + p_{NO}^p + p_O^p + p_{NO^+}^p \quad (32)$$

Additionally, from charge conservation,

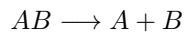
$$p_{NO^+}^p = p_{e^-}^p \quad (33)$$

There are seven species, and only three equations. Hence it is necessary to calculate the Equilibrium constants of each of the individual reactions for the remaining four equations.

1. Equilibrium constant K_p

Equilibrium constant of pressure can be computed from the internal partition function of each of the species.

Consider the equation:



The equilibrium constant for this is given by:³

$$Kp_{AB} = \frac{p_A^p p_B^p}{p_{AB}^p} = \left(\frac{2\pi m_A m_B kT}{m_{AB} h^2} \right)^{\frac{3}{2}} kT \frac{Q_A Q_B}{Q_{AB}} e^{\frac{-D_0}{kT}} \quad (34)$$

This gives the additional four equations. But the resulting seven equations are non-linear. They have to be solved using some root finding method with proper initial guess. The ratio of partial pressure of each of the components with the total pressure gives the mole fraction of the species. The mass fraction can be obtained by multiplying each term with its corresponding molar mass. The weighted sum of the same provides the specific heat of the mixture.

D. Curve fits for thermodynamic properties

The variation of thermodynamic properties for a given pressure and a range of temperatures is found out with the above methodology. The functions such as Cp are approximated using a seventh order polynomial with degree ranging from -2 to 4. That is:

$$\frac{C_p(T)}{R} = a_1T^{-2} + a_2T^{-1} + a_3 + a_4T + a_5T^2 + a_6T^3 + a_7T^4 \quad (35)$$

This produces good results if the domain is restricted.⁶ Control points are identified where there is a drastic change in the slope of the function. Curve fits are obtained for each domain as:

$$f(x) = \sum_{j=1}^7 a_j x^{j-3} \quad (36)$$

$$\min \left[\sum_{i=1}^n (y_i - f(x_i))^2 \right] \quad (37)$$

A suitable optimization routine is used to obtain the parameters.

III. Results

Due to the vastness of the data, only selected plots are shown for demonstrative purposes. The hard numbers can be obtained from tables generated by the author.

A. Partition function

The internal partition function for Nitrogen is shown below. It was calculated using equation 18 as there was some discrepancies in the spectroscopic data of Nitrogen. The difference obtained can be attributed to this along with an uncertainty as to the number of electronic levels considered by Capitelli.² The internal function of Oxygen is also shown below. The variation in values between present computation and Capitelli can be attributed additionally to the errors due to interpolation. Spline interpolation was used to save computational time.

B. Specific heat

The variation of specific heats for Nitrogen and Oxygen are shown below. The variations in the partition functions amplify in Cp.

C. Composition and equilibrium constant

The variation is again shown for Nitrogen and Oxygen. The comparison is done with Barklem.¹

D. Mixture thermodynamic properties

The thermodynamic properties of air are shown below.

E. Curve fits

Tabulated below are the curve fits for specific heat of Nitrogen. All the other tables are similar in nature.

Table 1. Curve-fit for Cp/R of Nitrogen

Coefficients	100K-2500K	2500K-8000K	8000K-18000K	18000K-22000K	22000K-30000K
A1	1.6637946e+00	3.1651973e-03	-1.5047620e-04	-1.0190640e-03	-8.7801382e-04
A2	-2.4434158e+00	7.2433194e-04	-6.8701167e-04	2.2599813e-03	1.1746039e-03
A3	3.5623756e+00	-2.5806735e-03	-1.4242511e-03	7.3481886e-04	3.2102028e-04
A4	-6.5831490e-04	3.7917134e-03	1.9003863e-03	-1.8408490e-03	1.1638909e-03
A5	1.8386176e-06	-1.1494748e-06	-3.0988192e-07	3.5645687e-07	-4.4102326e-08
A6	-9.9656386e-10	1.4890337e-10	2.2491837e-11	-1.7551239e-11	2.7304215e-13
A7	1.6856875e-13	-6.9215436e-15	-5.3935701e-16	2.7018838e-16	5.3915305e-18

IV. Conclusions and discussions

This report apart from producing data pertaining to relevant thermodynamic parameters, more importantly has documented data of spectroscopic data and partition function data along with curve fits for air. This can come in handy to other enthusiasts.

1. The reason for an error of sometimes upto 10% can be attributed to the fact that the electronic levels considered in computations such as these is a arbitrary.
2. The cut-off criterion for some of the ions is based on the electronic energy decrement which is again taken as a parameter or arbitrarily fixed.
3. Care has to be taken to verify that Jmax has converged for each iteration. This was unfortunately not done and could have contributed to some of the variation between this report and Capitelli's.
4. A lot of the literature shows a wide range of values. The numbers got out of this report lie somewhere in between.
5. Discrepancies arise mostly at temperatures greater than about 10000K. Most of the work done so far are upto 10000K. Results match closely up till that range. Only after does the uncertainty creep in.

Acknowledgments

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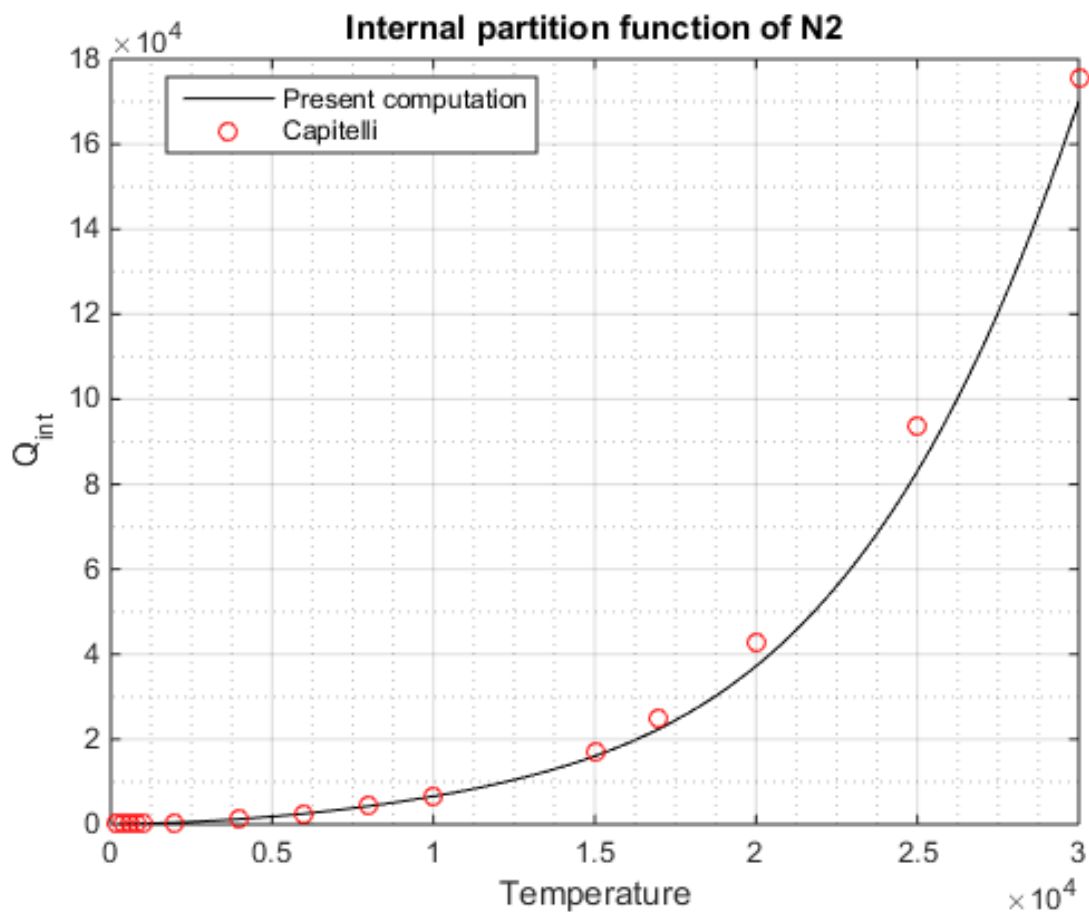


Figure 1. From direct summation of approximated formula.

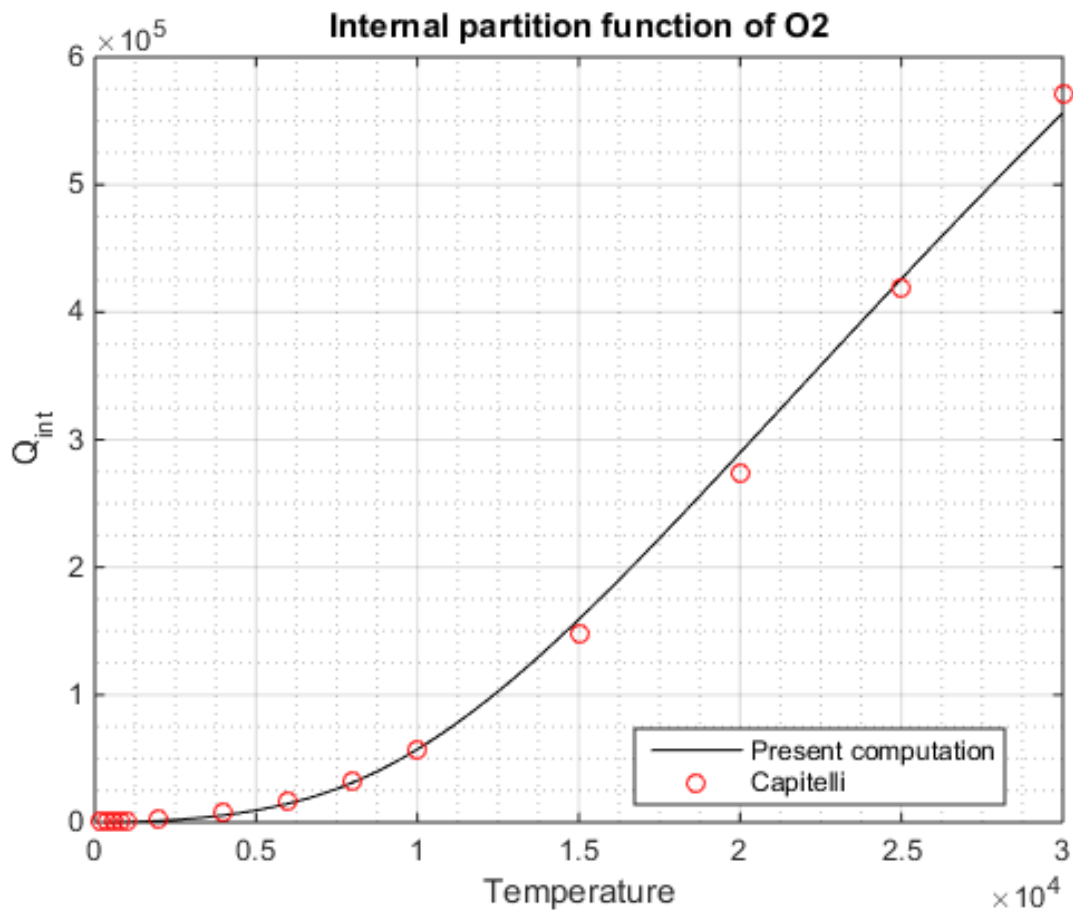


Figure 2. From direct summation.

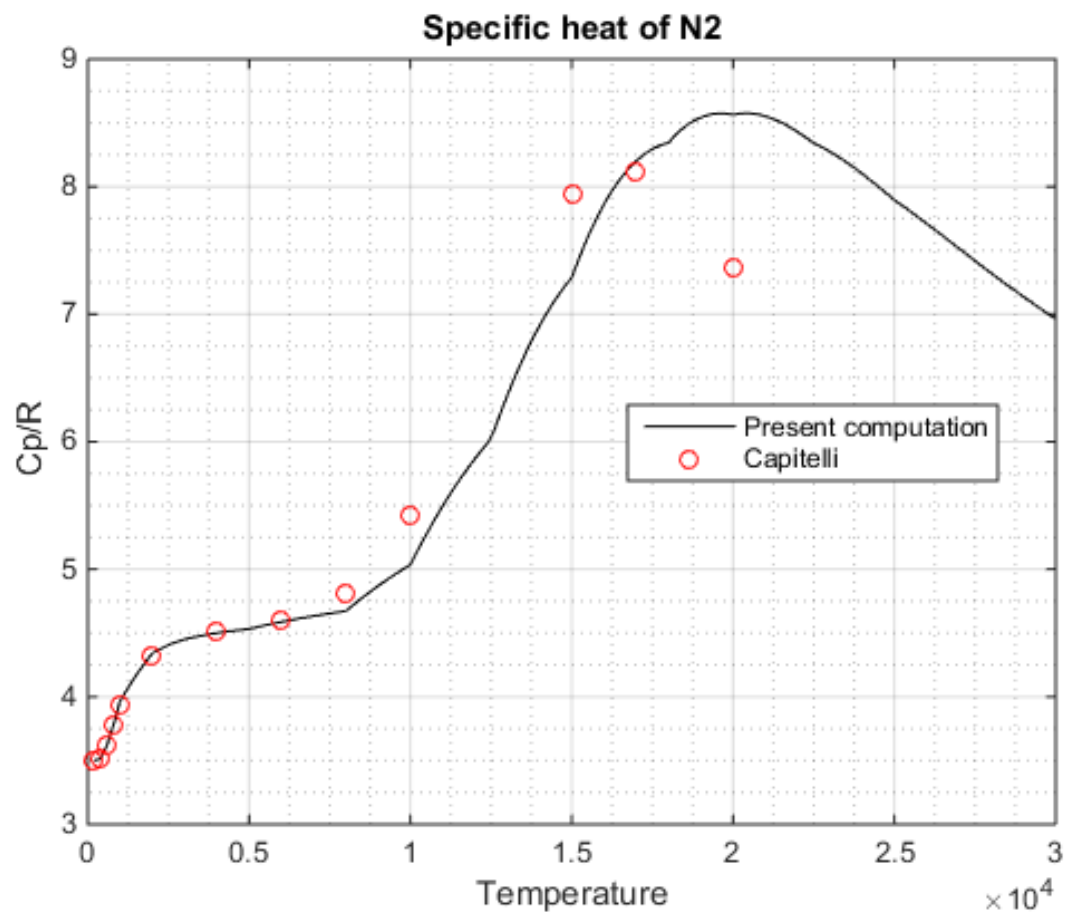


Figure 3. Using direct summation of approximated formula.

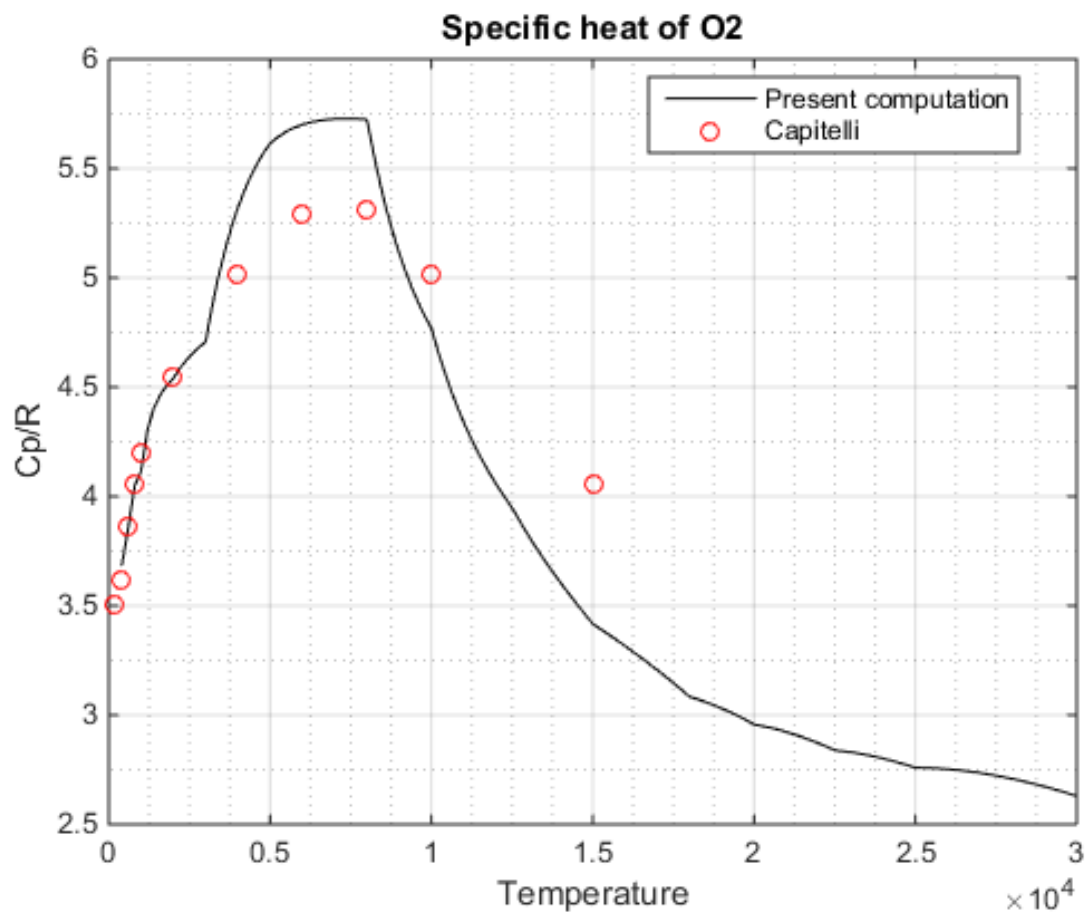


Figure 4. Using direct summation of approximated formula.

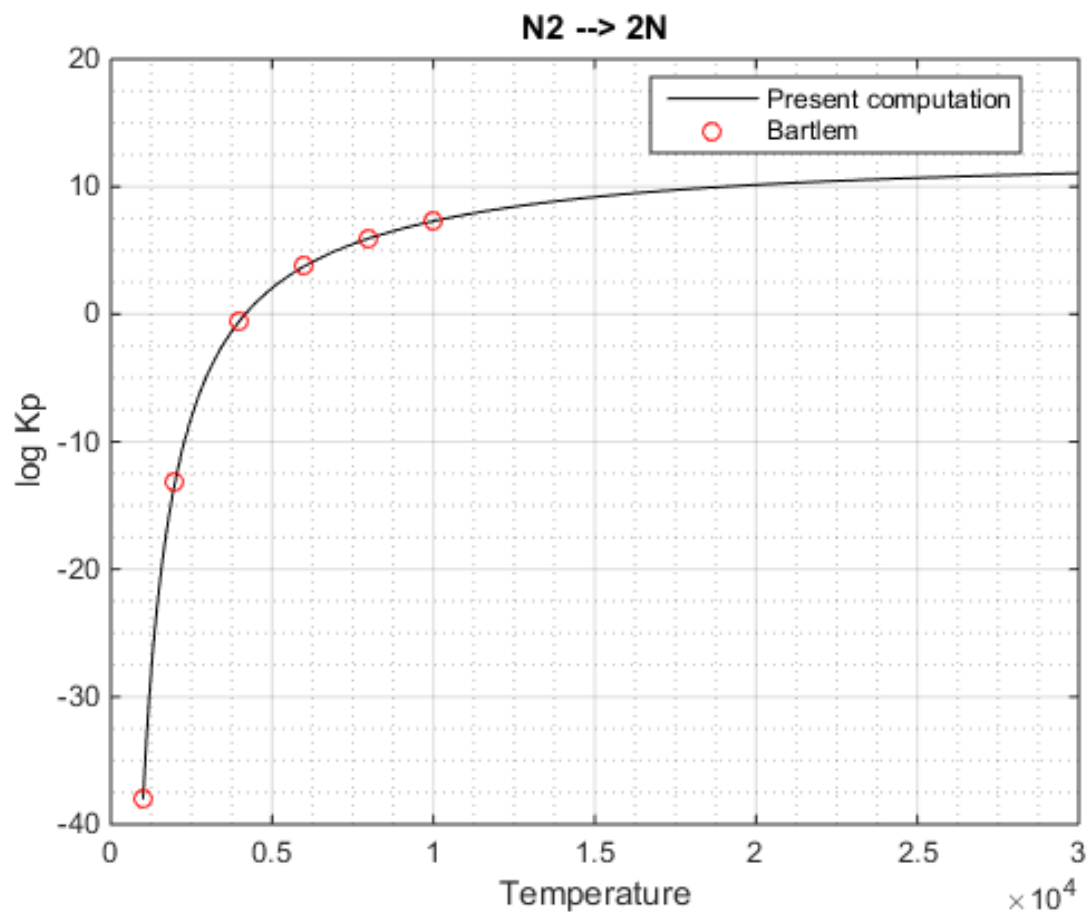


Figure 5. Using direct summation of approximated formula.

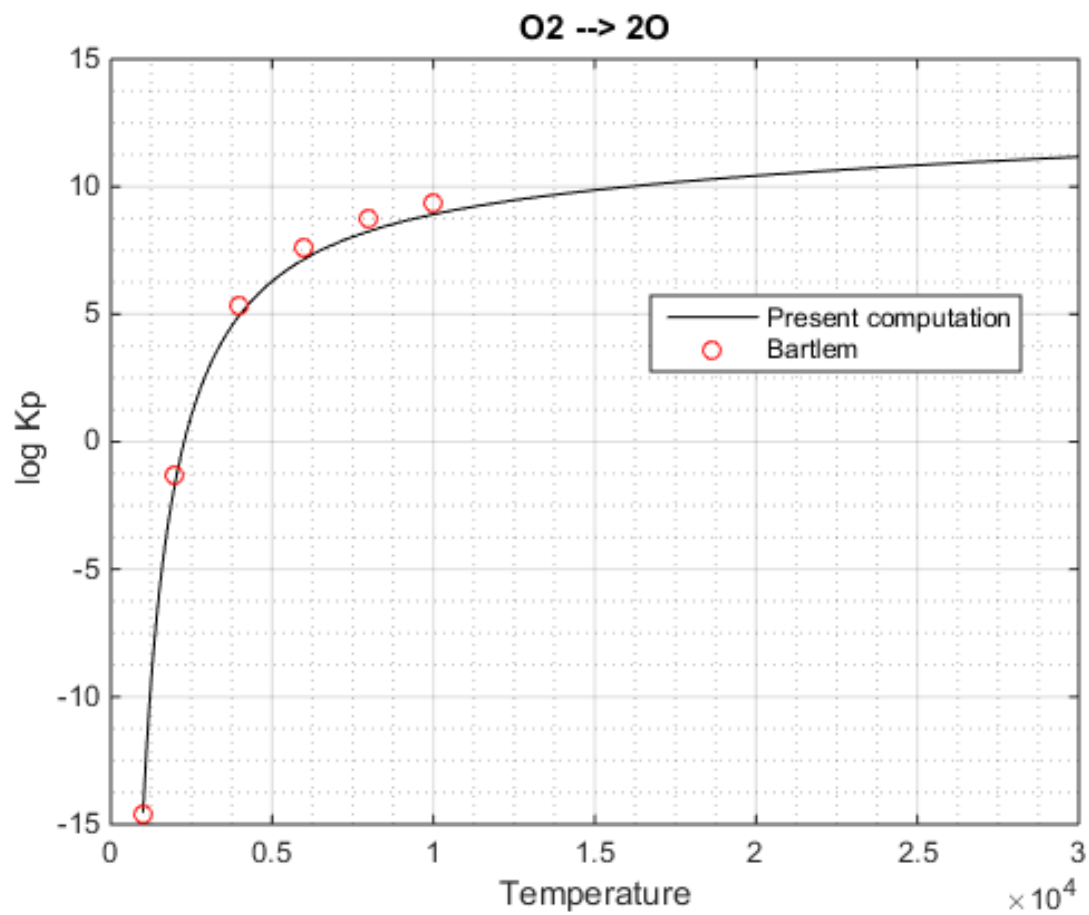


Figure 6. Using direct summation of approximated formula.

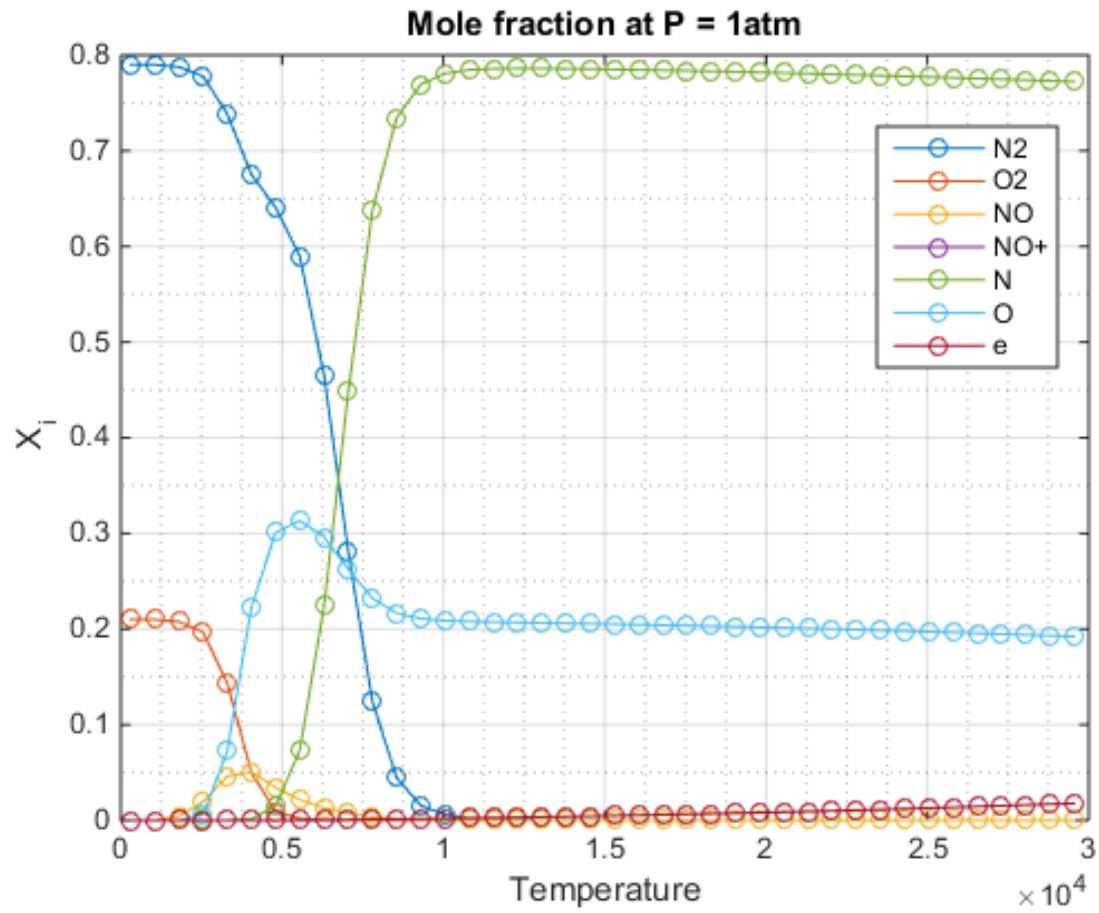


Figure 7. It can be seen that the molar fraction of the charged species is much less than N and O. But the dissociation of Nitrogen and Oxygen is almost complete.

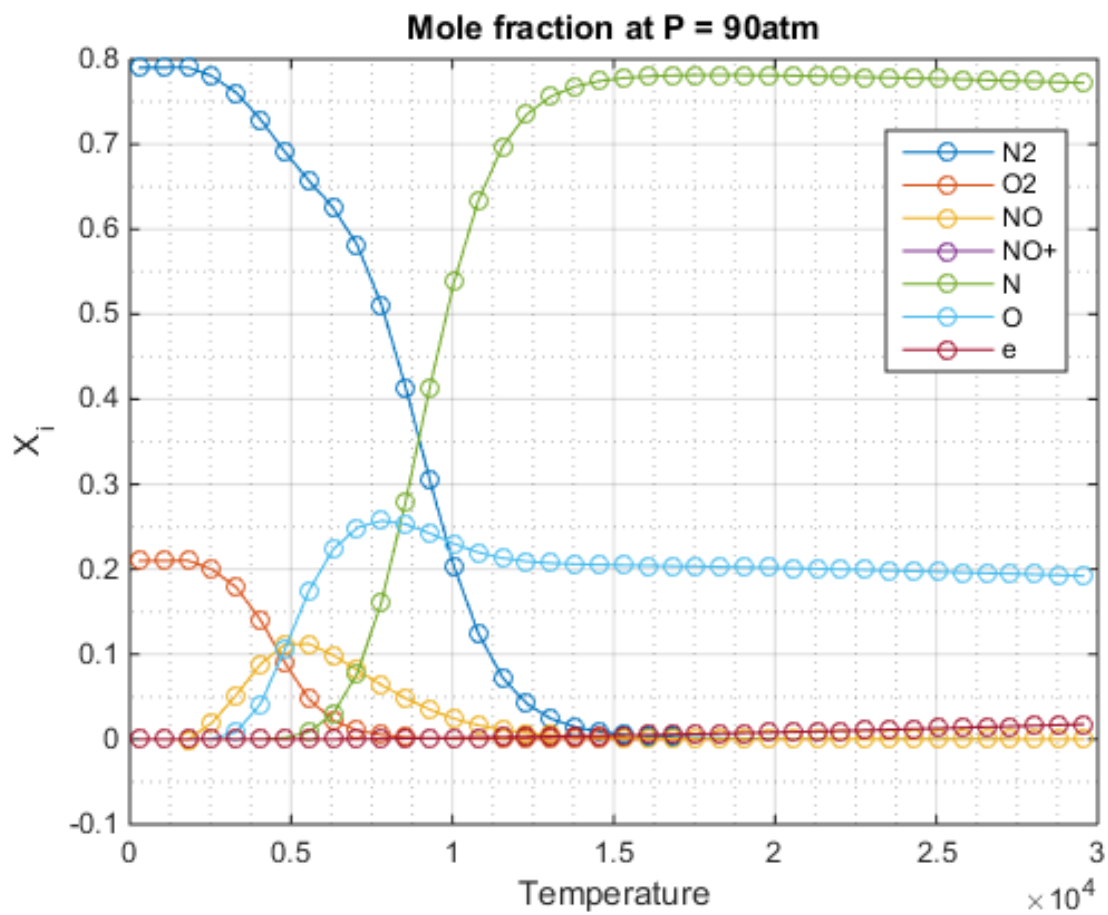


Figure 8. The higher pressure suppresses dissociation as expected from the Le Chatelier's principle.

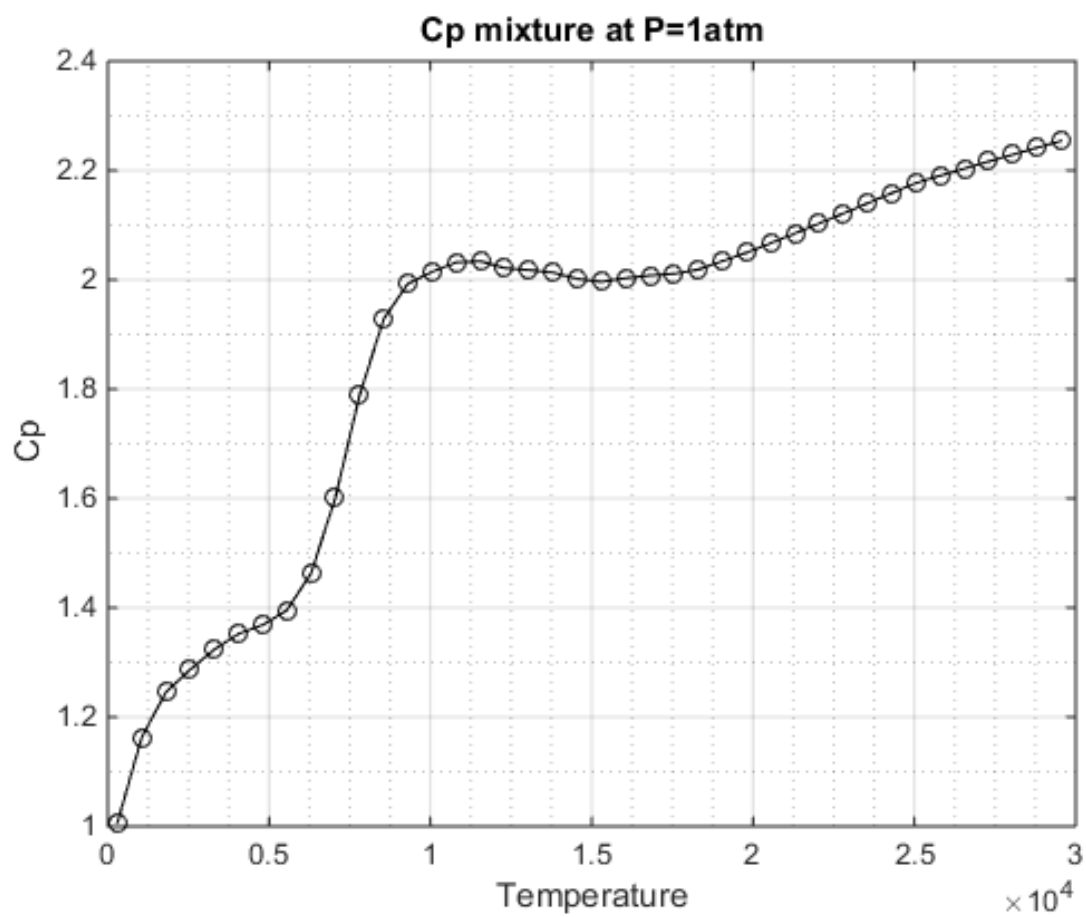


Figure 9. Spline interpolated from spline interpolated partition function.

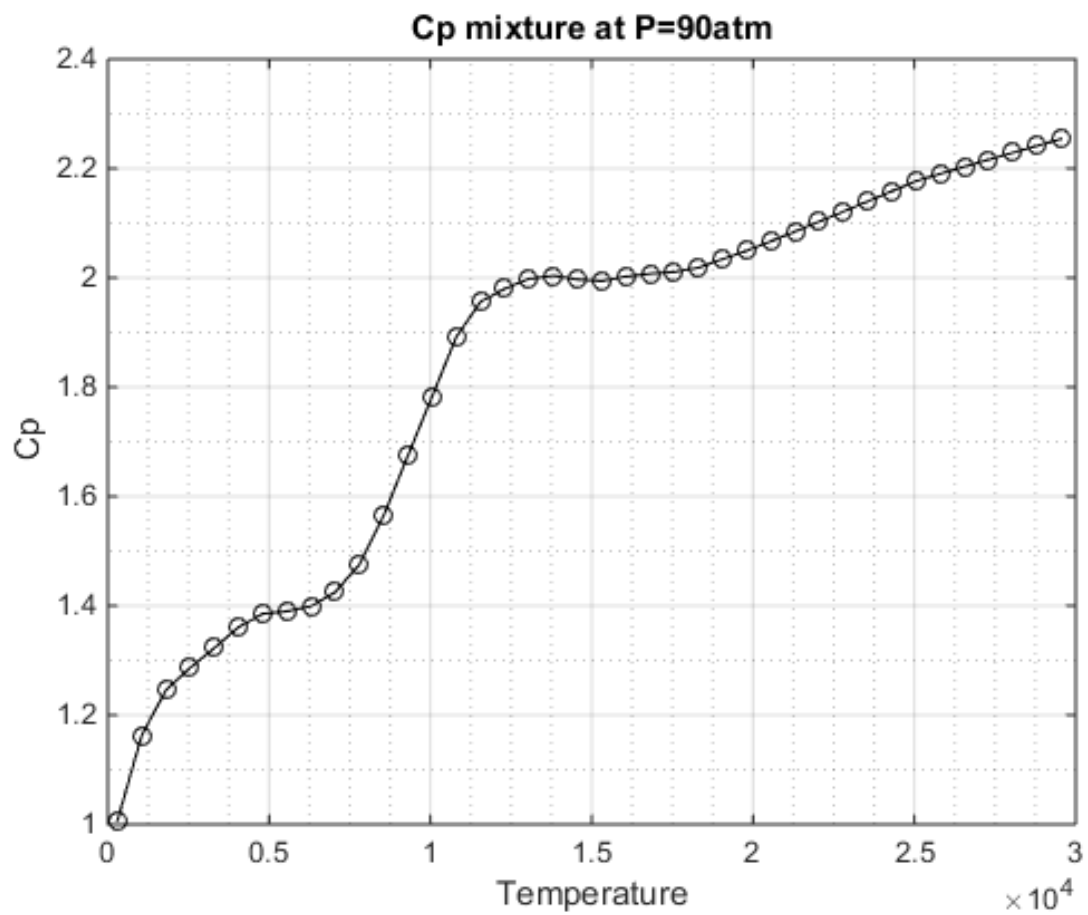


Figure 10. Spline interpolated from spline interpolated partition function.