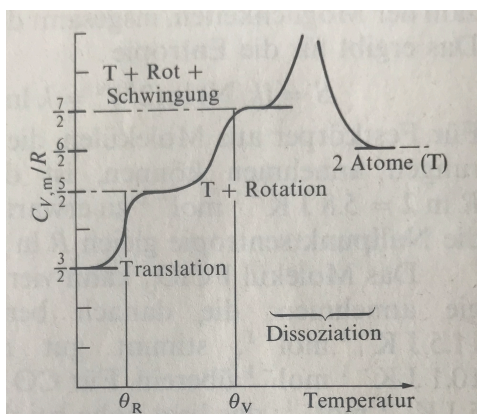


Problem 20: Heat capacity of HCl

The picture below (which is Abb. 22-6 in P.W. Atkins *Physikalische Chemie* (3rd edition) VCH (1986)) illustrates the general temperature dependence of the isochoric molar capacity $C_V^{(1)}$ of a diatomic molecule (per mol). We want to, at least partially, calculate this curve for HCl.



Produce a graph of $C_V^{(1)}/k_B$ for HCl in the temperature range between 0.1 and 10^5 K (cf. Aufgabe 20 in R. Hentschke *Statistische Mechanik* Wiley-VCH (2004)). Assume that $\text{HCl} \equiv {}^1\text{H}^{35}\text{Cl}$ is a linear rotor with the equilibrium internuclear separation $r_o = 127.45$ pm. Further assume $C_{V,trans}^{(1)}/k_B = 3/2$ in the entire T -range and a vibrational wave number 2990.95 cm^{-1} . State explicitly the values you use for T_{rot} and T_{vib} .

(6 points)

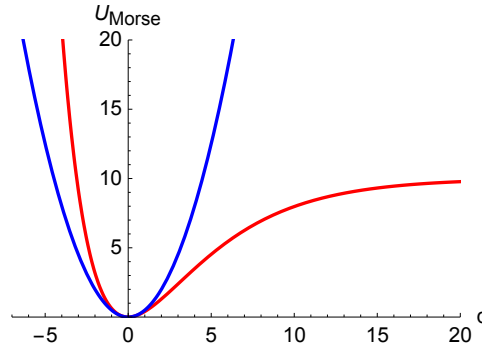
Problem 21: Harmonic vs. Morse oscillator

The Morse potential,

$$U_{Morse} = D_o(1 - \exp[-a q])^2, \quad (1)$$

is a phenomenological internuclear potential energy function for diatomic molecules. Here q is the deviation of the internuclear separation from its equilibrium value. U_{Morse} for $D_o = 10$ and $a = 1/\sqrt{2D_o}$ is shown by the red line in the figure. Taylor expansion of U_{Morse} at $q = 0$ and using again $a =$

$1/\sqrt{2D_o}$ yields the harmonic oscillator potential $U_{Morse}(q) \approx q^2/2$ shown by the blue line in the figure. Note that the Morse potential allows the dissociation of the molecule since the depth of the potential well, D_o , is finite.



In the present units the energy eigenvalues of the harmonic oscillator potential (blue curve) are $\epsilon_{osc} = n + 1/2$ and $n = 0, 1, 2, \dots$. The energy eigenvalues of the Morse potential can also be calculated analytically (e.g. chapter 6 in S.-H. Dong *Factorization method in quantum mechanics*. Springer (2007)). They follow via the condition

$$2s = \nu - 2n - 1, \quad (2)$$

where $s = \sqrt{2(D_o - \epsilon_{Morse})/a^2}$, $\nu = \sqrt{8D_o/a^2}$ and $n = 0, 1, \dots, n_{max}$.

Calculate the heat capacity for the Morse potential $c_V \equiv C_V/k_B$ vs. $t = T/T_{vib}$ in the range $0 < t < 4$ using $a = 1/\sqrt{2D_o}$ and $D_o = 10$. Plot your result together with the corresponding heat capacity for the harmonic oscillator approximation. Indicate the high temperature limit of the harmonic oscillator by a dotted line also in the range $0 < t < 4$. Interpret the difference between the two heat capacities, i.e. why is c_V of the Morse potential larger than c_V of the oscillator for intermediate t but decreases towards zero for $t \rightarrow \infty$?

(6 points)

Problem 22: Second virial coefficient of Argon

Let's assume that the interaction between Argon atoms in the gas phase is well described by the (pairwise) Lennard-Jones (LJ) potential

$$u_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (3)$$

Using the experimental data provided in the table, obtain the LJ parameters ϵ/k_B (in units of Kelvin) and σ (in units of Å) for Argon. Provide a graph showing the comparison between $B_2^{theo}(T)$ and $B_2^{exp}(T)$ vs. temperature T . Hint: Do not try to solve the B_2 -integral analytically. Use a numerical solver instead.

T/K	B_2/cm^3mol^{-1}
100	-184
280	-19
460	3
640	13
820	18
1000	21

(6 points)