On the 100th Anniversary of the Sackur–Tetrode Equation

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Entropy of a monoatomic ideal gas:

$$S(E, V, N) = kN \left(\frac{3}{2} \ln \frac{E}{N} + \ln \frac{V}{N} + s_0 \right)$$

1912: Otto Sackur and Hugo Tetrode independently determined

$$s_0 = \frac{3}{2} \ln \frac{4\pi m}{3h^2} + \frac{5}{2}$$

Sackur–Tetrode equation =
absolute entropy of a monoatomic ideal gas

Contents

Motivation

Absolute entropy:
Boltzmann (1875), Planck (1900):

$$S = k \ln W + \text{const.}$$

Argument: Nernst's heat theorem (1906)
(third law of thermodynamics)
$\Rightarrow$ S should be calculable without any additive constant
Massive particles: phase space volume of "elementary cells" unknown
Sackur (1911): Entropy of a monoatomic ideal gas as a function of the volume of elementary cell

Tetrode's derivation

Ansatz: n degrees of freedom $\Rightarrow$

Elementary domains of volume $\sigma = \delta q_1\, \delta p_1 \cdots \delta q_n\, \delta p_n = (zh)^n$

N identical particles $\Rightarrow$

$$S = k \ln \frac{W'}{N!}$$

W' = number of configurations in phase space
Total admissible volume in phase space space given E, V, N:

$$\mathcal{V}(E, V, N) = \int \mathrm{d}^3 x_1 \int \mathrm{d}^3 p_1 \cdots \int \mathrm{d}^3 x_N \int \mathrm{d}^3 p_N$$

with

$$\frac{1}{2m} \left(\vec{p}_1^{\,2} + \cdots + \vec{p}_N^{\,2} \right) \leq E$$

Tetrode's derivation

Dilute gas:

$$S = k \ln \frac{\mathcal{V}(E,V,N)}{(zh)^{3N} N!} \quad \text{with} \quad \mathcal{V}(E,V,N) = \frac{(2\pi m E)^{\frac{3N}{2}}\, V^N}{\Gamma\left(\frac{3N}{2}+1\right)}$$

Stirling's formula: $\ln n! \simeq n(\ln n - 1)$

Tetrode's result:

$$S(E,V,N) = kN\left(\frac{3}{2}\ln\frac{E}{N} + \ln\frac{V}{N} + \frac{3}{2}\ln\frac{4\pi m}{3(zh)^2} + \frac{5}{2}\right)$$

Sackur's derivation

Following derivation in paper of October 1912

- Partioning of energy space into cubes:
  $n_k \Delta\varepsilon \leq \varepsilon_k < (n_k + 1)\Delta\varepsilon \; (k = x, y, z)$
  Energy associated with i-th cube:

$$\varepsilon_i = (n_x + n_y + n_z)\Delta\varepsilon$$

- Observation time τ during which collisions are negligible
  Ansatz:

$$N_i = Nf(\varepsilon_i)\,(\tau\Delta\varepsilon)^3$$

- N atoms distributed over r cubes:

$$W = \frac{N!}{N_1!N_2!\cdots N_r!} \quad \text{with} \quad N = N_1 + N_2 + \cdots + N_r$$

Sackur's derivation

- Conditions:

$$\sum_i N_i = \sum_i N f(\varepsilon_i)\,(\tau\Delta\varepsilon)^3 = N$$
$$\sum_i N_i\,\varepsilon_i = \sum_i N f(\varepsilon_i)\,(\tau\Delta\varepsilon)^3\,\varepsilon_i = E$$

- Stationary point of $S = k \ln W$:

$$N_i = N\alpha e^{-\beta\varepsilon_i} \quad \text{and} \quad S = -3kN\ln(\tau\Delta\varepsilon) - kN\ln\alpha + k\beta E$$

- Referring to Sommerfeld (1911): "smallest action that can take place in nature is given by Planck's constant"

$$\tau\Delta\varepsilon = h$$

- Integration over energy space:

$$\tau^3 \mathrm{d}\varepsilon_x \mathrm{d}\varepsilon_y \mathrm{d}\varepsilon_z = \frac{V}{N}\,\mathrm{d}p_x \mathrm{d}p_y \mathrm{d}p_z$$

Sackur's derivation

- Conditions: summation → integration ⇒

$$\beta = \frac{3N}{2E} \quad \text{and} \quad \alpha = \frac{N}{V}\left(\frac{3N}{4\pi mE}\right)^{3/2}$$

Sackur's result:

$$S(E,V,N) = kN\left(\frac{3}{2}\ln\frac{E}{N} + \ln\frac{V}{N} + \frac{3}{2}\ln\frac{4\pi m}{3h^2} + \frac{3}{2}\right)$$

Sackur misses one kN in entropy!
(in previous paper correct number 5/2)

Remarks: Sackur's derivation resembles derivation with canonical partition function

$$Z = \frac{Z_1^N}{N!}$$

$$Z_1 = \frac{1}{h^3} \int_{\mathcal{V}} d^3x \int d^3p \, \exp\left(-\beta \frac{\vec{p}^{\,2}}{2m}\right) = \frac{V}{\lambda^3} \quad \text{with} \quad \lambda = \frac{h}{\sqrt{2\pi mkT}}$$

λ = thermal de Broglie wave length $\Rightarrow$

$$S(T, V, N) = k(\ln Z + \beta E) = kN\left(\ln \frac{V}{\lambda^3 N} + \frac{5}{2}\right)$$

is identical with Tetrode's result upon substitution $E = \frac{3}{2}NkT$

Sackur's α related to Z_1: $\alpha = N/(h^3 Z_1)$

Test of the Sackur–Tetrode equation

Planck's constant h known from black-body radiation

- Sackur: Test of $\delta q\, \delta p = h$
- Tetrode: Determination of z in $\delta q\, \delta p = zh$

Usage of data on phase transition liquid–vapor of mercury

Idea:

$$\underbrace{L(T)}_{\text{exp.}} = T\left(\underbrace{s_{\text{vapor}}(T, \bar{p}(T))}_{\text{ST equation}} - \underbrace{s_{\text{liquid}}(T)}_{\text{exp.+theory}} \right)$$

L . . . . molar latent heat
s . . . . . . absolute molar entropy
$\bar{p}$ . . . . vapor pressure

Test of the Sackur–Tetrode equation

Sackur–Tetrode equation:

$R = kN_A$, λ = thermal de Broglie wave length

$$s_{\mathrm{vapor}} = R\left(\ln \frac{kT}{\bar{p}(T)\,\lambda^3(T)} + \frac{5}{2}\right)$$

Entropy of liquid:

In good approximation entropy and heat capacity of liquids pressure-independent

$$s_{\mathrm{liquid}}(T) = \int_0^T \mathrm{d}T' \, \frac{c_p(T')}{T'}$$

Kirchhoff's equation:

Δc_p = difference of molar heat capcity across coexistence curve

$$\frac{\mathrm{d}L}{\mathrm{d}T} \simeq \Delta c_p \quad \text{with} \quad \Delta c_p = \frac{5}{2}R - c_p^{\mathrm{liquid}}$$

Test of the Sackur–Tetrode equation

Vapor pressure:

$$\ln \bar{p}(T) = -\frac{L(T)}{RT} + \ln \frac{(2\pi m)^{3/2}(kT)^{5/2}}{h^3} + \frac{5}{2} - \int_0^T dT' \frac{c_p(T')}{RT'}$$

Test of Sackur–Tetrode equation:

Suitable temperature intervall $[T_1, T_2]$
corresponding to vapor pressure interval $[\bar{p}_1, \bar{p}_2]$
Experimental input: $L(T_0)$, c_p^{liquid} and $\bar{p}$ in intervall
Experimental + theoretical:

$$\int_0^{T_0} dT' \frac{c_p(T')}{T'}$$

Test of the Sackur–Tetrode equation

Entropy of a liquid (part 1):

$$\mathrm{d}s(T,p) = \frac{c_p}{T}\mathrm{d}T - \left.\frac{\partial v}{\partial T}\right|_p \mathrm{d}p$$

Reference point (T_0, p_0) at coexistence curve
Third law of thermodynamics $\Rightarrow$

$$s_{\text{liquid}}(T_0, p_0) = \int_0^{T_0} \mathrm{d}T' \, \frac{c_p(T', p_0)}{T'}$$
$$= \int_0^{T_m} \mathrm{d}T' \, \frac{c_p^{\text{solid}}(T', p_0)}{T'} + \frac{L_m(T_m)}{T_m} + \int_{T_m}^{T_0} \mathrm{d}T' \, \frac{c_p^{\text{liquid}}(T', p_0)}{T'}$$

c_p^{solid} from model by Nernst (1911), $c_p^{\text{solid}} \stackrel{T\to 0}{\longrightarrow} 0$ exponentially

Entropy of a liquid (part 2):

s_{liquid} at $(T, \bar{p})$ by $(T_0, p_0) \to (T, \bar{p})$ along coexistence curve

$$\mathrm{d}s = \frac{c_p^{\text{liquid}}}{T}\,\mathrm{d}T - \alpha v\,\mathrm{d}\bar{p} \quad \text{with} \quad \alpha = \frac{1}{v}\frac{\partial v}{\partial T}\bigg|_p$$

$\alpha =$ isobaric expansion coefficient

Numerical estimation:

$\alpha \simeq 1.8 \times 10^{-4}\,\mathrm{K}^{-1}$, $v/N_A \sim 10\,\text{Å}^3$, $c_p^{\text{liquid}} \simeq 28\,\mathrm{J\,mol^{-1}\,K^{-1}}$
Temperature intervall: $T_1 = T_m = -39\,°\mathrm{C}$, $T_2 \sim 200\,°\mathrm{C}$
Vapor pressure intervall: $\bar{p}_1 \simeq 3 \times 10^{-8}\,\mathrm{bar}$, $\bar{p}_2 \sim 0.2\,\mathrm{bar}$

One has to compare $c_p^{\text{liquid}} \ln \frac{T_2}{T_1}$ with $\alpha v(\bar{p}_2 - \bar{p}_1)$

$\alpha v \times 1\,\mathrm{bar} \sim 1 \times 10^{-4}\,\mathrm{J\,mol^{-1}}$!!!

Test of the Sackur–Tetrode equation

Test with modern data:
CODATA Key Values for Thermodynamics
Standard State: $T_0 = 298.15\,\mathrm{K}$, $p_0 = 1\,\mathrm{bar}$

$$L_0(\mathrm{Hg}) = 61.38 \pm 0.04\ \mathrm{kJ\,mol^{-1}}, \quad s_0(\mathrm{Hg}) = 75.90 \pm 0.12\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

CRC Handbook of Chemistry and Physics:
Vapor pressure and c_p^{liquid} data between
$T_1 = -38.84\,^\circ\mathrm{C}$ and $T_2 = 200\,^\circ\mathrm{C}$
CODATA: $h = 6.62606957(29) \times 10^{-34}\ \mathrm{Js}$
Fit of z to mercury data: $h \to z \times (\text{mean value of } h)$

$$z = 1.003 \pm 0.004(L_0) \pm 0.005(s_0)$$

Concluding remarks

Papers:

1. O. Sackur, *The application of the kinetic theory of gases to chemical problems* (received October 6, 1911):
   - S of a monoatomic ideal gas as a function of the size of the elementary cell
2. O. Sackur, *The meaning of the elementary quantum of action for gas theory and the computation of the chemical constant* (no "received date", must have been written in spring 1912):
   - Postulate: size of elementary cell is h^n
   - Absolute entropy S of a monoatomic ideal gas
   - Vapor pressure over a solid
   - Comparison with data on neon and argon
     numerical results not really satisfying and conclusive

Concluding remarks

iii. H. Tetrode, *The chemical constant and the elementary quantum of action* (received March 18, 1912):
   - Derivation of S, assuming size $(zh)^n$ of elementary cell
   - Fit of z by using data on the vapor pressure of liquid mercury, due to some numerical mistakes $z \approx 0.07$

iv. H. Tetrode, erratum to *The chemical constant and the elementary quantum of action* (received July 17, 1912):
   - Correction of formulas and numerics, $z \sim 1$
   - Reference to the papers of Sackur by noting that the formula for S has been developed by both of them at the same time

v. O. Sackur, *The universal meaning of the so-called elementary quantum of action* (received October 19, 1912):
   - Good agreement ($\pm 30\%$) with data on Hg vapor pressure
   - Comments on paper by Tetrode

Concluding remarks

Historical context: Thermodynamics, Planck's constant and early applications

1900 Planck: black body radiation, Plank's constant

1905 Einstein: photoelectric effect

1906 Nernst: Third law of thermodynamics

1907 Einstein: Einstein model of heat capacity of solids

1907 Stark: minimal wavelength of X-rays

1911 Sommerfeld: "action in pure molecular processes"

1912 Debye: Debye model of solid

Concluding remarks

Subatomic physics:

- X-rays (Roentgen (1895))
- radioactivity (Becquerel (1896))
- electron (J.J. Thomson (1897))
- radium (Bémont, Curie, Curie (1898))
- half-life of ^{220}Ra (Rutherford (1900))
- atomic nucleus (Rutherford (1911))
- Bohr model of atom (Bohr (1913))

Concluding remarks

Achievement of Sackur and Tetrode:

- Absolute entropy of monoatomic ideal gas
- Quantization of phase space in classical statistical physics

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Otto Sackur: 1880–1914
Hugo Tetrode: 1895–1931

Concluding remarks

H.B.G. Casimir, NRC Handelsblad, February 23, 1984

Article about H. Tetrode: “Een vergeten genie”

Visit of Einstein and Ehrenfest

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"Meneer ontvangt niet"
Sir is not receiving guests