

Formulary of Thermodynamics

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ABSTRACT

Aims. Small sample of important and useful equations in Classical Thermodynamics

Methods. L^AT_EX 2_ε and class notes

Results. A nice two-column paper with formulas

0.1. Notation

- 2 $E > 0$ energy getting *absorbed* by the system in POV
- 3 $E < 0$ energy getting *emitted/discarded* by the system in
- 4 POV
- 5 Thus: $Q = U + W$ (IUPAC notation)

1. Constants and non-SI Units

1.1. non-SI Units

- 8 – atmosphere, pressure: 1 atm = 101325 Pa
- 9 – mercury millimeters, pressure: 1 mmHg = 133.32 Pa
- 10 – calorie, energy: 1 cal = 4.187 J
- 11 – big calorie, energy: 1 Cal = 1 kcal = 4186.799 J
- 12 – liters, volume: 1 l = $1 \cdot 10^{-3}$ m³

1.2. Constants

- 14 – R , ideal gas constant: $R = 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} = 0.0821 \frac{\text{l} \cdot \text{atm}}{\text{mol} \cdot \text{K}}$
- 15 – k_B , Boltzmann constant: $k_B = 1,38065 \cdot 10^{-23} \frac{\text{J}}{\text{K}}$
- 16 – N_A , Avogadro number: $N_A = 6.022 \cdot 10^{23} \frac{1}{\text{mol}}$
- 17 – σ , Stefan-Boltzmann constant: $\sigma = 5.6704 \cdot 10^{-8} \frac{\text{W}}{\text{m}^2 \text{K}^4}$

2. Principles

2.1. Zeroth Principle

20 Given two thermodynamic systems A and B , isolated from
21 each other and in contact through diathermal walls to a
22 thermodynamic system C , then, said T the temperature

$$T_B = T_C \vee T_A = T_C \implies T_A = T_B \quad (1)$$

2.2. First Principle

24 Internal energy U , heat Q , work W

$$\delta Q = dU + \delta W \quad (2)$$

2.3. Second Principle

26 Entropy S , reversible transformation

$$\delta Q = T dS \quad (3)$$

27 Entropy of the universe S_Ω , surroundings (ambient) entropy
28 S_a , Q_a ambient heat (with sign) [if Q_{abs} is the heat ab-
29 sorbed from the system in study, then $Q_a = -Q_{abs}$]

$$\Delta S_\Omega = \Delta S + \Delta S_a = \int \frac{1}{T} \delta Q + \frac{Q_a}{T_a} \geq 0 \quad (4)$$

3. Ideal Gases

Equation of state, p pressure, V volume, $R = 8.314$ J/K, T temperature, N particle number

$$pV = nRT = Nk_B T \quad (5)$$

n number of moles, N number of molecules, M molecular mass

$$n = \frac{m}{M} = \frac{N}{N_A} \quad (6)$$

In reversible transformations

$$dU = nc_v dT \quad (7)$$

4. Calorimetry

Specific heats for monoatomic gases:

- c_v , specific heat at constant volume, $c_v = \frac{3}{2}R$
- c_p , specific heat at constant pressure, $c_p = \frac{5}{2}R$
- γ , heat capacity ratio, $\gamma = \frac{c_p}{c_v}$

Note that

$$c_p = c_v + R \quad (8)$$

For n-atomic gases:

$$c^{(n)} = c + \frac{n}{2}R \quad (9)$$

For an ideal calorimeter, with m_w mass of water at T_w temperature and c_w specific heat, a substance with mass m_x and temperature T_x , then, with T_{eq} the equilibrium temperature

$$c_x = \frac{m_w c_w (T_w - T_{eq})}{m_x (T_{eq} - T_x)} \quad (10)$$

For a calorimeter of mass m_1 , with m_2 mass of water, then the equivalent mass is

$$m^* = \frac{m_2 (T_w - T_{eq})}{(T_1 - T_{eq})} - m_1 \quad (11)$$

The equilibrium temperature is

$$T_{eq} = \frac{(m_w + m^*) c_w T_w + m_x c_x T_x}{m_x c_x + (m_w + m^*) c_w} \quad (12)$$

51 For solids:

$$Q_s = mc_s \Delta T$$

52 Where

$$c_s = 3R$$

53 Therefore

$$\Delta S_s = mc_s \log \left(\frac{T_B}{T_A} \right)$$

54 4.1. Phase Changes

55 For phase changes, λ latent heat, m mass

$$Q = m\lambda$$

56 For pressure p

$$p(T) = p_0 e^{\frac{m\lambda}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right)}$$

57 5. Transformations

58 Transformation $A \rightarrow B$:

59 – Isobaric: $p_A = p_B$

60 – Isochoric: $V_A = V_B$

61 – Isothermal: $T_A = T_B$

62 – Adiabatic: $p_A V_A^\gamma = p_B V_B^\gamma$, $T_A V_A^{\gamma-1} = T_B V_B^{\gamma-1}$

63 – Free expansion (irreversible): $T_A = T_B$, $Q_{AB} = 0$

64 Differentials from the first law

| Transformation | δQ | δW | dU |
|----------------|--|--------------------------|-----------|
| Isobaric | $nc_p dT$ | $nR dT$ | $nc_v dT$ |
| Isochoric | $nc_v dT$ | 0 | $nc_v dT$ |
| Isothermal | $\frac{nRT}{V} dV$ | $\frac{nRT}{V} dV$ | 0 |
| Adiabatic | 0 | $-nc_v dT$ | $nc_v dT$ |
| Polytropic | $n \left(\frac{R}{1-\alpha} + c_v \right) dT$ | $\frac{nR}{1-\alpha} dT$ | $nc_v dT$ |

65 Entropy variations

66 – Isobaric: $\Delta S = nc_p \log \left(\frac{T_B}{T_A} \right) = nc_p \log \left(\frac{V_B}{V_A} \right)$

67 – Isochoric: $\Delta S = nc_v \log \left(\frac{T_B}{T_A} \right) = nc_v \log \left(\frac{p_B}{p_A} \right)$

68 – Isothermal: $\Delta S = nR \log \left(\frac{V_B}{V_A} \right) = -nR \log \left(\frac{p_B}{p_A} \right)$

69 – Adiabatic: $\Delta S = 0$

70 – Free expansion (irr):

$$\Delta S = nR \log \left(\frac{V_B}{V_A} \right) = -nR \log \left(\frac{p_B}{p_A} \right)$$

6. Thermodynamic Cycles

(12) Cycle efficiencies, Q_{abs} heat absorbed by the machine, Q_{em} heat emitted by the machine

– η , efficiency: $\eta = \frac{|W|}{|Q_{abs}|}$

– COP_f , coefficient of prestaton (cooling):

$$COP_f = \frac{|Q_{abs}|}{|W|}$$

– COP_p , coefficient of prestaton (heating):

$$COP_p = COP_f + 1 = \frac{|Q_{em}|}{|W|}$$

(14) Table of cycles, T_{min}/T_{max} low/high heat reservoir temperature, $r = \frac{V_{max}}{V_{min}}$ compression ratio, $r_p = \frac{p_{max}}{p_{min}}$

| Cycle | Transformations | η |
|----------|-----------------------------------|-------------------------------------|
| Carnot | 2 adiabats, 2 isotherms | $1 - \frac{T_{min}}{T_{max}}$ |
| Otto | 2 adiabats, 2 isochores | $1 - r^{1-\gamma}$ |
| Diesel | 2 adiabats, 1 isochor, 1 isotherm | |
| Brayton | 2 adiabats, 2 isobars | $1 - r_p^{\frac{1-\gamma}{\gamma}}$ |
| Stirling | 2 isotherms, 2 isochors | |

(16) 7. Heat Transfer

7.1. Conduction

κ thermal conductivity, S surface area, t time

$$\frac{Q}{St} = q = -\kappa \frac{dT}{dx} \quad (17)$$

7.2. Convection

$$h = \kappa/x$$

$$\frac{Q}{St} = q = h\Delta T \quad (18)$$

For multiple surfaces

$$h = \frac{1}{\frac{1}{h_1} + \dots + \frac{1}{h_n}} \quad (19)$$

7.3. Irradiation

Energy E , σ Stefan Boltzmann constant, ε emittivity

$$\frac{1}{S} \frac{dE}{dt} = \sigma \varepsilon T^4 \quad (20)$$

8. Kinetic Theory

Energy equipartition

$$E = \frac{3}{2} N k_B T \quad (21)$$

Average velocities, M molecular mass, m particle mass, S_p particle cross sectional surface

$$\langle v \rangle, \text{ average velocity: } \langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}} = \sqrt{\frac{8RT}{\pi M}}$$

$$v_{qm}, \text{ square root mean velocity: } v_{qm} = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3RT}{M}}$$

| | | | |
|-----|---|--|------|
| 105 | – v_m , most probable velocity: $v_m = \sqrt{\frac{2k_B T}{m}} = \sqrt{\frac{2RT}{M}}$ | 9.6. C_p - C_v Equations | 128 |
| 106 | | First $c_p - c_v$ equation | 129 |
| 107 | – v_{rel} , relative velocity: $v_{rel} = \sqrt{\frac{16k_B T}{\pi m}} = \sqrt{\frac{16RT}{\pi M}} =$ | | |
| 108 | $\sqrt{2} \langle v \rangle$ | $c_p - c_v = -T \left(\frac{\partial V}{\partial T} \right)_p \left(\frac{\partial p}{\partial V} \right)_T$ | (30) |
| 109 | | | |
| 110 | – Z , number of collisions per second: $Z = \frac{N}{V} \langle v \rangle S_p$ | Second $c_p - c_v$ equation | 130 |
| 111 | | | |
| 112 | – λ , mean free path: $\lambda = \frac{\langle v \rangle}{Z}$ | | |

113 9. Fundamental Equations

114 9.1. Van der Waals Equation of State

115 a pressure correction parameter, b volume correction pa-
116 rameter

$$\left(p + a \frac{n^2}{V^2} \right) (V - nb) = nRT \quad (22)$$

117 9.2. Potentials

118 Gibbs energy G , enthalpy H , free energy F , internal energy
119 U

$$dG = dU + d(pV) - TdS = dH - TdS = dF + d(pV) \quad (23)$$

120 9.3. Maxwell Relations

$$\begin{aligned} \left(\frac{\partial T}{\partial V} \right)_S &= - \left(\frac{\partial p}{\partial S} \right)_V \\ \left(\frac{\partial T}{\partial p} \right)_S &= \left(\frac{\partial V}{\partial S} \right)_p \\ \left(\frac{\partial p}{\partial T} \right)_V &= \left(\frac{\partial S}{\partial V} \right)_T \\ \left(\frac{\partial V}{\partial T} \right)_p &= - \left(\frac{\partial S}{\partial p} \right)_T \end{aligned} \quad (24)$$

121 9.4. TdS Equations

122 First TdS

$$TdS = nc_v dT + T \left(\frac{\partial p}{\partial T} \right)_V dV \quad (25)$$

123 Second TdS

$$TdS = nc_p dT - T \left(\frac{\partial V}{\partial T} \right)_p dp \quad (26)$$

124 Third TdS

$$TdS = nc_v \left(\frac{\partial T}{\partial p} \right)_V dp + nc_p \left(\frac{\partial T}{\partial V} \right)_p dV \quad (27)$$

125 9.5. Energy Equations

126 First energy equation

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_V - p \quad (28)$$

127 Second energy equation

$$\left(\frac{\partial U}{\partial p} \right)_T = -T \left(\frac{\partial V}{\partial T} \right)_p - p \left(\frac{\partial V}{\partial p} \right)_T \quad (29)$$