Formulary of Thermodynamics

1

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ABSTRACT

Aims. Small sample of important and useful equations in Classical Thermodynamics
Methods. LaTeX 2_ε and class notes
Results. A nice two-column paper with formulas

0.1. Notation

$E > 0$ energy getting *absorbed* by the system in POV

$E < 0$ energy getting *emitted/discarded* by the system in POV

Thus: $Q = U + W$ (IUPAC notation)

1. Constants and non-SI Units

1.1. non-SI Units

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

1.2. Constants

− R, ideal gas constant: $R = 8.314 \frac{\text{J}}{\text{mol·K}} = 0.0821 \frac{\text{l·atm}}{\text{mol·K}}$
− k_B, Boltzmann constant: $k_B = 1,38065 \cdot 10^{-23} \frac{\text{J}}{\text{K}}$
− N_A, Avogadro number: $N_A = 6.022 \cdot 10^{23} \frac{1}{\text{mol}}$
− 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

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

$$T_B = T_C \ \lor \ T_A = T_C \implies T_A = T_B \tag{1}$$

2.2. First Principle

Internal energy U, heat Q, work W

$$\delta Q = \mathrm{d}U + \delta W \tag{2}$$

2.3. Second Principle

Entropy S, reversible transformation

$$\delta Q = T\mathrm{d}S \tag{3}$$

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

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

3. Ideal Gases

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

$$pV = nRT = Nk_BT \tag{5}$$

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

$$n = \frac{m}{M} = \frac{N}{N_A} \tag{6}$$

In reversible transformations

$$\mathrm{d}U = nc_v\mathrm{d}T \tag{7}$$

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

$$c_p = c_v + R \tag{8}$$

For n-atomic gases:

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

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

$$c_x = \frac{m_wc_w(T_w - T_{eq})}{m_x(T_{eq} - T_x)} \tag{9}$$

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

$$m^\star = \frac{m_2(T_w - T_{eq})}{(T_1 - T_{eq})} - m_1 \tag{10}$$

The equilibrium temperature is

$$T_{eq} = \frac{(m_w + m^\star)c_wT_w + m_xc_xT_x}{m_xc_x + (m_w + m^\star)c_w} \tag{11}$$

51 For solids:

$$Q_s = mc_s\Delta T \tag{12}$$

52 Where

$$c_s = 3R \tag{13}$$

53 Therefore

$$\Delta S_s = mc_s \log\left(\frac{T_B}{T_A}\right) \tag{14}$$

4.1. Phase Changes

55 For phase changes, λ latent heat, m mass

$$Q = m\lambda \tag{15}$$

56 For pressure p

$$p(T) = p_0 e^{\frac{m\lambda}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)} \tag{16}$$

5. Transformations

58 Transformation $A \to B$:

59   – Isobaric: $p_A = p_B$

61   – Isochoric: $V_A = V_B$

63   – Isothermal: $T_A = T_B$

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

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

68 Differentials from the first law

Transformation	δQ	δW	$\mathrm{d}U$
Isobaric	$nc_p\mathrm{d}T$	$nR\mathrm{d}T$	$nc_v\mathrm{d}T$
Isochoric	$nc_v\mathrm{d}T$	0	$nc_v\mathrm{d}T$
Isothermal	$\frac{nRT}{V}\mathrm{d}V$	$\frac{nRT}{V}\mathrm{d}V$	0
Adiabatic	0	$-nc_v\mathrm{d}T$	$nc_v\mathrm{d}T$
Polytropic	$n\left(\frac{R}{1-\alpha}+c_v\right)\mathrm{d}T$	$\frac{nR}{1-\alpha}\mathrm{d}T$	$nc_v\mathrm{d}T$

5.1. Entropy variations

70 Entropy calculations in transformations

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

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

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

77   – Adiabatic: $\Delta S = 0$

78   – Free expansion: $\Delta S = nR \log\left(\frac{V_B}{V_A}\right) = -nR \log\left(\frac{p_B}{P_A}\right)$

79 Generic entropy variations

80   – $\Delta S(V,T) = nc_v \log\left(\frac{T_B}{T_A}\right) + nR \log\left(\frac{V_B}{V_A}\right)$

81   – $\Delta S(T,p) = nc_p \log\left(\frac{T_B}{T_A}\right) - nR \log\left(\frac{p_B}{p_A}\right)$

82   – $\Delta S(p,V) = nc_p \log\left(\frac{V_B}{V_A}\right) + nc_v \log\left(\frac{p_B}{p_A}\right)$

6. Thermodynamic Cycles

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 prestation (cooling): $\mathrm{COP}_f = \frac{|Q_{ass}|}{|W|}$

  – COP_p, coefficient of prestation (heating): $\mathrm{COP}_p = \mathrm{COP}_f + 1 = \frac{|Q_{em}|}{|W|}$

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	

7. Heat Transfer

7.1. Conduction

κ thermal conductivity, S surface area, t time

$$\frac{Q}{St} = q = -\kappa \frac{\mathrm{d}T}{\mathrm{d}x} \tag{17}$$

7.2. Convection

$$h = \kappa/x$$

$$\frac{Q}{St} = q = h\Delta T \tag{18}$$

For multiple surfaces

$$h = \frac{1}{\frac{1}{h_1} + \cdots + \frac{1}{h_n}} \tag{19}$$

7.3. Irradiation

Energy E, σ Stefan Boltzmann constant, ε emittivity

$$\frac{1}{S}\frac{\mathrm{d}E}{\mathrm{d}t} = \sigma\varepsilon T^4 \tag{20}$$

8. Kinetic Theory

Energy equipartition

$$E = \frac{3}{2}Nk_BT \tag{21}$$

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

  – $\langle v \rangle$, average velocity: $\langle v \rangle = \sqrt{\frac{8k_BT}{\pi m}} = \sqrt{\frac{8RT}{\pi M}}$

  – v_{qm}, square root mean velocity: $v_{qm} = \sqrt{\frac{3k_BT}{m}} = \sqrt{\frac{3RT}{M}}$

109   – v_m, most probable velocity: $v_m = \sqrt{\frac{2k_B T}{m}} = \sqrt{\frac{2RT}{M}}$

110
111   – v_{rel}, relative velocity: $v_{rel} = \sqrt{\frac{16k_B T}{\pi m}} = \sqrt{\frac{16RT}{\pi M}} =$
112    $\sqrt{2}\langle v \rangle$

113
114   – Z, number of collisions per second: $Z = \frac{N}{V}\langle v \rangle S_p$

115
116   – λ, mean free path: $\lambda = \frac{\langle v \rangle}{Z}$

117   9. Fundamental Equations

118   *9.1. Van der Waals Equation of State*

119 a pressure correction parameter, b volume correction pa-
120 rameter

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

121   *9.2. Potentials*

122 Gibbs energy G, enthalpy H, free energy F, internal energy
123 U

$$dG = dU + d(pV) - TdS = dH - TdS = dF + d(pV) \tag{23}$$

124   *9.3. Maxwell Relations*

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

125   *9.4. TdS Equations*

126 First TdS

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

127 Second TdS

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

128 Third TdS

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

129   *9.5. Energy Equations*

130 First energy equation

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

131 Second energy equation

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

132   *9.6. Cp-Cv Equations*

133 First $c_p - c_v$ equation

$$c_p - c_v = -T\left(\frac{\partial V}{\partial T}\right)_p^2 \left(\frac{\partial p}{\partial V}\right)_T \tag{30}$$

134 Second $c_p - c_v$ equation

$$\frac{c_p}{c_v} = \gamma = \frac{\left(\frac{\partial p}{\partial V}\right)_S}{\left(\frac{\partial p}{\partial V}\right)_T} \tag{31}$$