# Golden sheet Autumn 2011, ver. 1.0

## 1 Thermodynamics

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|---|---|
| 1. law of thermodynamics: | $dU = q + w \overset{\text{QS}}{=} q - pdV$ |
| 2. law of thermodynamics (isolated system): | $\Delta S \geq 0\,, \qquad S = k_B \ln \Omega$ |
| 3. law of thermodynamics: | $T \to 0 \Rightarrow S \to 0, C_x \to 0$ |
| Entropy growth by delivering heat: | $dS \geq \frac{q}{T}$ |
| | $dS = \frac{q}{T}$ (Quasistatic) |
| Equipartition theorem: | $U = \frac{f}{2} N k_B T, \quad$ f = # degrees of freedom |

Thermodynamic potentials:

| Potential | Differential form | Maxwell relation |
|---|---|---|
| $U$ | $dU = +TdS - PdV + \mu dN$ | $\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial P}{\partial S}\right)_{V,N}$ |
| $H = U + PV$ | $dH = +TdS + VdP + \mu dN$ | $\left(\frac{\partial T}{\partial P}\right)_{S,N} = +\left(\frac{\partial V}{\partial S}\right)_{P,N}$ |
| $F = U - TS$ | $dF = -SdT - PdV + \mu dN$ | $\left(\frac{\partial S}{\partial V}\right)_{T,N} = +\left(\frac{\partial P}{\partial T}\right)_{V,N}$ |
| $G = U + PV - TS = \mu N$ | $dG = -SdT + VdP + \mu dN$ | $\left(\frac{\partial S}{\partial P}\right)_{T,N} = -\left(\frac{\partial V}{\partial T}\right)_{P,N}$ |

Linear response functions (dN=0):

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| Specific heat | $C_V = \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$ | $C_P = \left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$ |
| Thermal expansion coefficient | $\alpha_P = +\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ | $\alpha_S = -\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_S$ |
| Compressibility | $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ | $\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$ |
| Bulk modulus | $K_T = -V\left(\frac{\partial P}{\partial V}\right)_T = \frac{1}{\kappa_T}$ | $K_S = -V\left(\frac{\partial P}{\partial V}\right)_S = \frac{1}{\kappa_S}$ |
| Pressure coefficient | $\beta_V = \left(\frac{\partial P}{\partial T}\right)_V$ | $\beta_S = \left(\frac{\partial P}{\partial T}\right)_S$ |

$dV = 0$: Isochoric; $dP = 0$: Isobaric; $dT = 0$: Isothermal;
$Q = 0$: Adiabatic; $dS = 0$: Isentropic (Adiabatic + Quasistatic)

## 2 Statistical mechanics

In thermal equilibrium with the surroundings: $p(s) = \frac{e^{-\beta E(s)}}{Z}, \quad \beta \equiv \frac{1}{k_B T}$
Partition function: $Z = \sum_s e^{-\beta E(s)} \quad (\Rightarrow \sum_s p(s) = 1)$
Average value of variable $A$: $\langle A \rangle = \sum_s A(s) p(s) = \sum_s A(s) \frac{e^{-\beta E(s)}}{Z}$
Mean energy: $U = \langle E \rangle = -\frac{\partial \ln(Z)}{\partial \beta} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}$
Helmholtz free energy: $F = -k_B T \ln(Z)$
Distinguishable, independent “particles”: $Z = Z_1 \cdot Z_2 \cdot Z_3 \cdot Z_4 \cdot ... \qquad (E = E_1 + E_2 + E_3 + E_4 + ...)$
Indistinguishable, independent “particles”: $Z = Z_1^N / N!$

## 3 Ideal-gas

Equation of state: $PV = Nk_B T = nRT$
Thermal energy: Only quadratic degrees of freedom; $U = f/2 N k_B T$.

## 4 Math

Binomial-coefficient: $\binom{N}{n} = \frac{N!}{n!(N-n)!}$
Stirling's approximation: $\ln(N!) \approx N\ln(N) - N \quad (N >> 1)$
Taylor expansion: $f(x) = f(a) + f'(a)(x-a) + \frac{f''(a)}{2!}(x-a)^2 + \frac{f'''(a)}{3!}(x-a)^3 + ...$
$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} + ...$
$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + ...$
$\sin(x) = x - \frac{x^3}{3!} + \frac{x^5}{5!} - ...$
$\cos(x) = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - ...$
$\frac{1}{1-x} = 1 + x + x^2 + x^3 + x^4 + ...$
$(1+x)^\alpha = \sum_{n=0}^{\infty} \binom{\alpha}{n} x^n$, hvor $\binom{\alpha}{n} = \frac{\alpha(\alpha-1)(\alpha-2)...(\alpha-n+1)}{n!}$

$\int_0^\infty x^n \exp(-ax^2)dx = I(n,a), \quad \frac{\partial I(n,a)}{\partial a} = -I(n+2,a)$

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| $I(0,a) = \frac{1}{2}\sqrt{\pi}a^{-1/2}$ | $I(2,a) = \frac{1}{4}\sqrt{\pi}a^{-3/2}$ | $I(4,a) = \frac{3}{8}\sqrt{\pi}a^{-5/2}$ |
| $I(1,a) = \frac{1}{2}a^{-1}$ | $I(3,a) = \frac{1}{2}a^{-2}$ | $I(5,a) = a^{-3}$ |

$Z$ is a function of $X$ and $Y$ ($Z = Z(X,Y)$),
$Y$ is a function of $X$ and $Q$ ($Y = Y(X,Q)$):

$$dZ = \left(\frac{\partial Z}{\partial X}\right)_Y dX + \left(\frac{\partial Z}{\partial Y}\right)_X dY \qquad \text{[Total differential]}$$

$$\left(\frac{\partial Z}{\partial X}\right)_Y = \left[\left(\frac{\partial X}{\partial Z}\right)_Y\right]^{-1} \qquad \text{[The inverse of the derivative]}$$

$$\left(\frac{\partial Z}{\partial X}\right)_Y = \left(\frac{\partial Z}{\partial Q}\right)_Y \left(\frac{\partial Q}{\partial X}\right)_Y \qquad \text{[The chain rule]}$$

$$-1 = \left(\frac{\partial Z}{\partial X}\right)_Y \left(\frac{\partial X}{\partial Y}\right)_Z \left(\frac{\partial Y}{\partial Z}\right)_X \qquad \text{[``The fake chain rule'']}$$

$$\left(\frac{\partial}{\partial X}\left(\frac{\partial Z}{\partial Y}\right)_X\right)_Y = \left(\frac{\partial}{\partial Y}\left(\frac{\partial Z}{\partial X}\right)_Y\right)_X \qquad \text{[Exchange of order of differentiation]}$$

$$\left(\frac{\partial Z}{\partial X}\right)_Q = \left(\frac{\partial Z}{\partial X}\right)_Y + \left(\frac{\partial Z}{\partial Y}\right)_X \left(\frac{\partial Y}{\partial X}\right)_Q \qquad \text{[Exchange of fixed variable]}$$

## 5 Constants

$k_B = 1.381 \cdot 10^{-23}$ J/K $= 8.617 \cdot 10^{-5}$ eV/K $\qquad R = 8.315$ J/(mol K)
$N_A = 6.022 \cdot 10^{23}$
$h = 6.626 \cdot 10^{-34}$ J s $= 4.136 \cdot 10^{-15}$ eV s
1 atm $= 1.013$ bar $= 1.013 \cdot 10^5$ N/m$^2$ $= 1.013 \cdot 10^5$ Pa
1 eV $= 1.602 \cdot 10^{-19}$ J
1 u $= 1.661 \cdot 10^{-27}$ kg