

5. Canonical Statistics

5.1 Statistical thermodynamics

• preparations

$$\beta = 1 / k_B T \quad (5.1)$$

$$\frac{d}{dT} = \left(\frac{d\beta}{dT} \right) \frac{d}{d\beta} = -k_B \beta^2 \frac{d}{d\beta} \quad (5.2)$$

$$\ln x! \approx x \ln x - x \quad (\text{Stirling's approximation}) \quad (5.3)$$

for an ensemble of N indistinguishable particles:

$$Q = q^N / N! \quad (5.4a)$$

$$\ln Q \approx N(\ln q - \ln N + 1) \quad (5.4b)$$

Q : ensemble partition function, q : molecular partition function

⟨Thermodynamic functions⟩

$$U - U(0) = - \left(\frac{\partial \ln Q}{\partial \beta} \right)_V = -N \left(\frac{\partial \ln q}{\partial \beta} \right)_V \quad (5.5)$$

$$S = \frac{U - U(0)}{T} + k_B \ln Q = \frac{U - U(0)}{T} + Nk_B (\ln q - \ln N + 1) \quad (5.6)$$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V \quad (5.7)$$

• (A.1)~(A.20) in handout-5

[Exercise-5] Calculate the ideal-gas entropy of the following gases at 298 K and 1 bar and compare them with experimental values.

• atomic weights (most abundant isotopes) [amu] – C:12.0 O:16.0 Ar:40.0

• $k_B = 0.6950 \text{ cm}^{-1} \text{ K}^{-1}$

	B / cm^{-1}	$h\nu / \text{cm}^{-1}$	${}^mS_{\text{exp}} / R$
(1) Ar			18.62
(2) CO	1.92	2140	23.77
(3) O ₂ (${}^3\Sigma_g^-$)	1.44	1560	24.67

(answer)

translation: (A.2b) at 298 K, 1 bar $\rightarrow {}^mS_{\text{trans}} / R = 1.5 \ln(m / \text{amu}) + 13.091$

rotation: (A.5) at 298 K $\rightarrow {}^mS_{\text{rot}} / R = 1 + \ln(207.1 / \sigma B)$

vibration: (A.8) with $x = h\nu / 207.1$

electronic: (A.20) $\rightarrow$ only for O₂

${}^mS / R$	trans	rot	(trans+rot)	elec	(trans+rot+elec)	vib	(total)
(1) Ar	18.624						
(2) CO	18.089	5.681	(23.770)			0.000 ₃₇	(23.770)
(3) O ₂	18.289	5.275	(23.564)	1.099	(24.663)	0.004 ₅₇	(24.668)

• $\rightarrow$ used for checking quantum chemical calculations

Problem-5.1

Calculate the ideal-gas entropy (S) and isovolume heat capacity (C_V) of CO_2 at 298 K and 1 bar.

- Vibrational frequencies [cm^{-1}] (degeneracy): 1333, 667(2), 2349
 - $r(\text{C-O}) = 1.162 \text{ \AA}$
-

5.2 Transition state theory (TST)**⟨Equilibrium constant⟩**

$$K_c \equiv \frac{\prod_{\text{prod}} c_j}{\prod_{\text{reac}} c_i} = \frac{\prod_{\text{prod}} Q_j^\circ}{\prod_{\text{reac}} Q_i^\circ} \exp\left(-\frac{\Delta E}{k_B T}\right) \quad (5.8)$$

⟨TST rate constant⟩

$$k = \frac{k_B T}{h} \frac{Q_\ddagger^\circ}{\prod_{\text{reac}} Q_i^\circ} \exp\left(-\frac{E_0}{k_B T}\right) \quad (5.9)$$

Problem-5.2

Calculate the rate constant for reaction $\text{O}(^3\text{P}) + \text{H}_2 \rightarrow \text{OH} + \text{H}$ at 500 and 1500 K.

- atomic weights (most abundant isotopes) [amu] – H:1.0 O:16.0
 - H_2 : $B = 59.3 \text{ cm}^{-1}$, $h\nu = 4162 \text{ cm}^{-1}$
 - transition state ($^3\Pi$): $r(\text{H-H}) = 0.893 \text{ \AA}$, $r(\text{O-H}) = 1.212 \text{ \AA}$
vibrational frequencies [cm^{-1}]: 1738, 839, 562
 - $E_0 = 51.9 \text{ kJ mol}^{-1}$
 - $k_B = 0.6950 \text{ cm}^{-1} \text{ K}^{-1}$
 - $k_B / h = 2.084 \times 10^{10} \text{ K}^{-1} \text{ s}^{-1}$
-