

Due WS+1d

Physical Chemistry II

Exercises 9

1. General Concepts

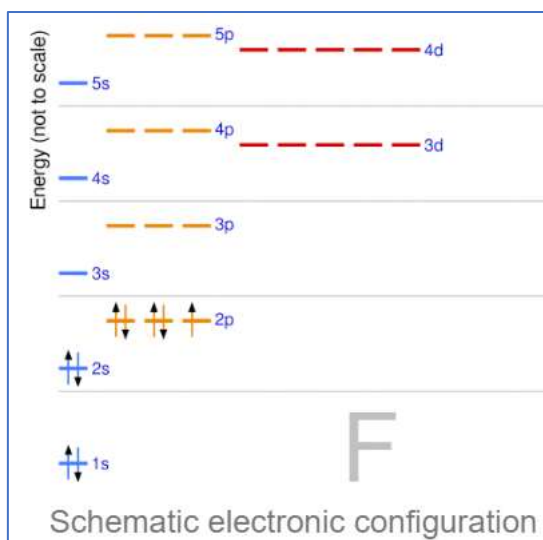
- Explain the effect on the quantum wave function of boundary conditions at the classically forbidden regions in space and the nature of the solutions.
- Discuss the equivalence and difference between the quantum wave function and the thermodynamic partition function. Illustrate the methods to generate observables from these functions (qu. traveling waves in a box).
- How do independent degrees of freedom of free gas particles affect the heat capacity of a gas. What does a higher heat capacity imply?
- Molecules have internal structure associated with a quantized energy spectrum. How does the heat capacity function $C_V(T)$ reflect that quantized spectrum?

2. Thermochemistry: Additivity of Chemical Reactions (Hess' Law)

The provided tables list relevant thermodynamic energies of formation, ΔH_f^0 , or of reaction, ΔH_{rxn}^0 , for several reactions.

- Write down the energy balance ΔH^0 for the reaction $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$
- Write down the energy balance ΔH^0 for the reaction
$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$$
- Calculate the heat evolved in the reaction $C(s) + O_2(g) \rightarrow CO_2(g)$ and justify your method.

3. Electronic Excitations



Atomic fluorine has the electronic configuration $1s^2 2s^2 2p^5$ in its ground state, $1s^2 2s^1 2p^6$ in its first excited state at 404cm^{-1} , and $1s^2 2s^2 2p^4 3s^1$ in its second excited state at $102,407\text{cm}^{-1}$. ($1\text{eV}=8,065\text{cm}^{-1}$, spins of paired electrons couple to $S_1 + S_2 = 0$)

- Write down the electronic degeneracy factors g_s for the fluor electronic ground, first, and second excited states.
- Write down the first 3 terms of the canonical PF.
- Estimate the populations of the electronic ground and first excited states for fluorine at $T=300\text{K}$
- Estimate the populations of the electronic ground and first excited states for fluorine at $T=2000\text{K}$.

4. Maxwell-Boltzmann Energy and Speed Distributions

The shape of the energy distribution of free gas particles in thermal equilibrium has been given in class.

- Determine the proper normalization of the MB energy distribution.
- Calculate the mean kinetic energy \bar{E} of the particles.
- Calculate the most probable kinetic energy of the particles.
- Calculate the mean speed \bar{v} of the particles.

5. Population of Molecular Rotational Energy Levels

Consider iodine vapor (I_2) at room temperature. The I_2 molecule has vibrational and rotational degrees of freedom. Relevant data for I_2 are listed in a table shown in class.

- Predict the mean and the most probable rotational angular momentum J to be observed for the molecule.
- Predict the probability for the first excited vibrational state of I_2 .

6. Surface Adsorption (AC)

Consider a canonical ensemble of N ideal gas particles (mass m) in a two-dimensional layer on the surface area F of a solid at room temperature. Assume that particle motion in the surface coordinates x and y is free and uncorrelated.

- Calculate the partition function Q_N as a function of surface coverage N/F .
- Calculate the energy per particle E/N .
- Calculate the Helmholtz surface tension $\sigma = -dA/dF$ of the adsorbed gas layer.

Species Name	Formula	$\Delta_f H^\circ(0\text{ K})$	$\Delta_f H^\circ(298.15\text{ K})$	Uncertainty	Units	Relative Molecular Mass	ATcT ID
Carbon monoxide	CO (g)	-113.802	-110.522	± 0.026	kJ/mol	28.01010 \pm 0.00085	630-08-0*0

Contribution (%)	Reaction	Measured Quantity
63.5	C (graphite) + CO ₂ (g) \rightarrow 2 CO (g)	$\Delta_r G^\circ(1165\text{ K}) = -33.545 \pm 0.058\text{ kJ/mol}$
4.3	C (graphite) + O ₂ (g) \rightarrow CO ₂ (g)	$\Delta_r H^\circ(298.15\text{ K}) = -393.464 \pm 0.024\text{ kJ/mol}$
3.6	CO ₂ (g) \rightarrow CO (g) + O+ (g)	$\Delta_r H^\circ(0\text{ K}) = 19.0701 \pm 0.0010 (\times 1.114)\text{ eV}$
3.1	CO (g) + 1/2 O ₂ (g) \rightarrow CO ₂ (g)	$\Delta_r H^\circ(303.15\text{ K}) = -282.974 \pm 0.116\text{ kJ/mol}$
2.3	C (graphite) + CO ₂ (g) \rightarrow 2 CO (g)	$\Delta_r G^\circ(1236.8\text{ K}) = -46.195 \pm 0.3\text{ kJ/mol}$
1.9	CO (g) + 1/2 O ₂ (g) \rightarrow CO ₂ (g)	$\Delta_r H^\circ(293.15\text{ K}) = -283.036 \pm 0.146\text{ kJ/mol}$
1.8	CO (g) + 1/2 O ₂ (g) \rightarrow CO ₂ (g)	$\Delta_r G^\circ(1173\text{ K}) = -180.655 \pm 0.150\text{ kJ/mol}$
1.7	C (graphite) + O ₂ (g) \rightarrow CO ₂ (g)	$\Delta_r H^\circ(298.15\text{ K}) = -393.468 \pm 0.038\text{ kJ/mol}$
1.7	C (graphite) + O ₂ (g) \rightarrow CO ₂ (g)	$\Delta_r H^\circ(298.15\text{ K}) = -393.462 \pm 0.038\text{ kJ/mol}$
1.2	CO ₂ (g) \rightarrow [CO]+ (g) + O (g)	$\Delta_r H^\circ(0\text{ K}) = 19.4687 \pm 0.0010 (\times 1.915)\text{ eV}$
1.1	C (graphite) + O ₂ (g) \rightarrow CO ₂ (g)	$\Delta_r H^\circ(298.15\text{ K}) = -94.051 \pm 0.011\text{ kcal/mol}$
0.8	CO (g) \rightarrow C+ (g) + O (g)	$\Delta_r H^\circ(0\text{ K}) = 22.3713 \pm 0.0015\text{ eV}$
0.8	C (graphite) + O ₂ (g) \rightarrow CO ₂ (g)	$\Delta_r H^\circ(298.15\text{ K}) = -393.462 \pm 0.056\text{ kJ/mol}$
0.6	C (graphite) + O ₂ (g) \rightarrow CO ₂ (g)	$\Delta_r H^\circ(298.15\text{ K}) = -393.498 \pm 0.062\text{ kJ/mol}$
0.6	C (graphite) + O ₂ (g) \rightarrow CO ₂ (g)	$\Delta_r H^\circ(303.15\text{ K}) = -393.447 \pm 0.064\text{ kJ/mol}$
0.5	CO (g) + H ₂ O (g) \rightarrow CO ₂ (g) + H ₂ (g)	$\Delta_r G^\circ(893\text{ K}) = -6.369 \pm 0.283\text{ kJ/mol}$