Name: __________________________

Instructions:

Check the exam to make sure that it contains exactly 6 different pages, including this one and a periodic table.

Some possibly useful equations and constants:

\[ h = 6.626 \times 10^{-34} \text{ J s} \quad \text{(Planck)} \]
\[ k_B = 1.381 \times 10^{-23} \text{ J K}^{-1} \quad \text{(Boltzmann)} \]
\[ N_A = 6.022 \times 10^{23} \text{ mol}^{-1} \quad \text{(Avogadro)} \]
\[ R = N_A k_B = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \]
\[ m_e = 9.11 \times 10^{-31} \text{ kg} \]
\[ e^x = 1 + x + \frac{x^2}{2!} + ... \quad (1-x)^1 = 1 + x + x^2 + ... \]
\[ q = \sum_n g_n e^{-\beta e_n}, \quad p_n = \frac{g_n e^{-\beta e_n}}{q} \]
\[ q_{\text{trans}} = \left( \frac{2\pi mk_b T}{h^2} \right)^{3/2} V \]
\[ q_{\text{rot}} = \left( \frac{k_B T}{\sigma c h B} \right) = \left( \frac{8\pi^2 I k_B T}{\sigma h^2} \right) \quad \text{where} \ I = \mu r^2 . \]
\[ q_{\text{vib}} = \left( 1 - e^{-h\nu/k_B T} \right)^{-1} \]
\[ Q = \frac{q}{N^1} \quad \text{(ideal gas)} \quad \ln(N!) \approx N \ln N - N \]
\[ U_{\text{trans}} = (3/2)Nk_B T \]
\[ C_V = dU/dT \quad C_V = \frac{5}{2} Nk_B + Nk_B \left( \frac{h\nu}{k_B T} \right)^2 \left( \frac{e^{h\nu/k_B T} - 1}{e^{h\nu/k_B T}} \right)^2 \]
\[ \Theta_V = \frac{h\nu}{k_B} \]
\[ S = k_B \ln Q + \frac{U}{T} \]
\[ S = nR \ln[(2\pi mk_B T/h)^{3/2}(V/N)e^{h\nu}] \]
\[ z_{ei} = \left( \frac{P N_A}{RT} \right)^{1/2} 2^{\alpha} \left( \frac{8RT}{\pi M} \right)^{1/2} \]
\[ \lambda = \frac{1}{\sqrt{2\alpha}} \left( \frac{RT}{PN_A} \right) \quad \text{(mean free path)} \]
\[ v_{\text{ave}} = \sqrt{\frac{8RT}{\pi M}} \quad v_{\text{rms}} = \sqrt{\frac{3RT}{M}} \quad v_{mp} = \sqrt{\frac{2RT}{M}} \]
\[ PV = nRT \]
Part 1. Write the letter of the answer which best satisfies each statement or question in the blank at the left. Please check your answers. Credit will only be given for the letter written in the blank (3 points each).

1. For which of the following energy levels are the spacings typically larger than $k_B T$ at room temperature?
   (A) translational  (B) rotational  (C) electronic  (D) nuclear spin
   - C

2. The constant volume molar heat capacity for all monatomic gases is
   (A) $3R/2$  (B) $5R/2$  (C) $R$  (D) $R/2$
   - A

3. Consider the probability distribution for $x$, $P(x) = (2\pi\sigma^2)^{-1/2}\exp[-(x-3)^2/2\sigma^2]$, where $x$ can take any value between $-\infty$ and $\infty$. The most probable value of $x$ is
   (A) -3  (B) 0  (C) 3  (D) $\sigma^2$
   - D

4. The mean free path of a molecule in a gas corresponds to
   (A) the diameter of the molecule  (B) the collision cross section  
   (C) the entropy  (D) the average distance a molecule travels between collisions
   - A

5. For which of the following molecules is the average speed highest at standard temperature and pressure?
   (A) $N_2$  (B) $O_2$  (C) NO  (D) $NO_2$
   - C

6. Consider $N$ molecules, each with two energy levels. The lower energy is 0 and the higher energy is $\varepsilon$. When $k_B T >> \varepsilon$, the average energy of the $N$ molecules is
   (A) 0  (B) $\varepsilon$  (C) $N\varepsilon/2$  (D) $N\varepsilon$
   - D

7. Which of the following noble gases in a 1.0 m$^3$ container at 298 K has the highest entropy?
   (A) He  (B) Ne  (C) Ar  (D) Kr
   - A

8. We use the energy levels of the following system to calculate the translational partition function for an ideal gas:
   (A) particle-in-a-box  (B) rigid rotor  
   (C) harmonic oscillator  (D) hydrogen atom
   - D

9. For which of the following degrees of freedom of a diatomic molecule is the partition function greatest at room temperature?
   (A) electronic  (B) vibrational  (C) rotational  (D) translational
   - B

10. Which of the following is greatest at 298 K?
    (A) $v_{mp}$ for He(g)  (B) $v_{rms}$ for He(g)  (C) $v_{mp}$ for Ar(g)  (D) $v_{rms}$ for Ar(g)
    - D
Part II. Short answer: Answer the following in the space provided. (12 points each)

1. Estimate the molar heat capacity, $C_{v,m}$, for $^{35}\text{Cl}_2$ gas at 200 K and at 10,000 K. The vibrational temperature of $^{35}\text{Cl}_2$ is 807 K.

\[
C_{v,m} = \frac{5}{2} R + R \left( \frac{\hbar \nu}{k_B T} \right)^2 \frac{e^{\frac{\hbar \nu}{k_B T}}}{e^{\frac{\hbar \nu}{k_B T}} - 1}. \]

At temperatures well below the vibrational temperature we can neglect the vibrational contribution in a rough estimate of the molar heat capacity. At temperatures at least 10 times the vibrational temperature the vibrational contribution is about $R$. Therefore at 200 K the heat capacity is about $(5/2) \, R$. At 10,000 K it is about $(7/2) \, R$.

2. Evaluate the translational partition function for $^{35}\text{Cl}_2$ confined in a 1.00 m$^3$ container at 298 K.

\[
q_{\text{translation}} = \left( \frac{2 \pi m k_B T}{\hbar^2} \right)^{3/2} V = \left( \frac{2 \pi \left( (70 \text{amu} / 6.02 \times 10^{23}) / 1000 \text{g/kg} \right) k_B T}{\hbar^2} \right)^{3/2} V = 5.7 \times 10^{32}
\]

3. Determine the temperature at which the average velocity, $v_{\text{avg}}$, for Kr is equal to that of Ne at 298 K.

\[
\sqrt{\frac{8 \pi T_{\text{Kr}}}{\pi M_{\text{Kr}}}} = \sqrt{\frac{8 \pi T_{\text{Ne}}}{\pi M_{\text{Ne}}}}. \quad \text{Therefore} \quad T_{\text{Kr}} = \frac{M_{\text{Kr}}}{M_{\text{Ne}}} T_{\text{Ne}} = \frac{(0.0838 \text{ kg mol}^{-1})}{(0.0202 \text{ kg mol}^{-1})} (298 \text{ K}) = 1240 \text{ K}
\]
Part III. Write your answer to the problems below in the space provided. Please show all work. Partial credit will be given based on work shown. (17 points each)

1. Determine the entropy for 1 mole of He(g) at 200 K in a volume of 100 cm$^3$. Then determine the entropy for 1 mole of Ne(g) at 200 K in a volume of 100 cm$^3$. Treat He and Ne as an ideal gas.

The entropy is given by, $S = nR \ln[(2\pi m k_B T/h^2)^{3/2}(V/N)e^{5/2}]$.

For 1 mole, $n = 1$ and $N = N_A$. $V = 100 \text{ cm}^3 = 1.0 \times 10^{-4} \text{ m}^3$.

$m_{Ar} = (4.00 \text{ g/mol})(1/6.022 \times 10^{23} \text{ mol}^{-1})(1 \text{ kg/1000 g}) = 6.64 \times 10^{-27} \text{ kg}$.

200 K:

$$S = nR \ln[(2\pi m k_B T/h^2)^{3/2}(V/N)e^{5/2}]$$

$$S = (1 \text{ mol})(8.314 \text{ J mol}^{-1}K^{-1}) \times$$

$$\ln[(2\pi(6.64 \times 10^{-27} \text{ kg}) (1.38 \times 10^{-23} \text{ J/K})(200 \text{ K})/(6.63 \times 10^{-34} \text{ J s})^{3/2}] \times$$

$$x (1.0 \times 10^{-4} \text{ m}^3)/(6.02 \times 10^{23} \text{ mol}^{-1}) e^{5/2}$$

$$S = 75.3 \text{ J K}^{-1}.$$

Ne at 200 K: Same calculation can be done for Ne, or we use a shortcut:

$$S_{Ne} - S_{He} = nR \ln m_{Ne}^{3/2} - nR \ln m_{He}^{3/2}$$

$$= (3/2)(1 \text{ mol})(8.314 \text{ J mol}^{-1}K^{-1}) \ln (20.18/4.00) = 20.2 \text{ J K}^{-1}$$

Therefore, for Ne at 200 K, $S = 95.5 \text{ J K}^{-1}$.
2. a) What is the molecular collision frequency, \( z_{11} \), for \( \text{N}_2 \) at 1.2 atm and a gas density of 52.0 moles/m\(^3\)? The collisional cross section for \( \text{N}_2 \) is \( 4.3 \times 10^{-19} \) m\(^2\). (10 points)

We estimate \( T \) using ideal gas law,

\[
T = \frac{PV}{nR} = \frac{P}{(n/V)R} = \frac{1.2 \text{ atm}}{(52.0 \text{ mol m}^{-3})(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1})(10^{-3} \text{ m}^3)} = 281 \text{ K}
\]

\[
z_{11} = \left( \frac{PN_A}{RT} \right)^{1/2} \sqrt{2} \alpha \left( \frac{8RT}{\pi M} \right)\]

\[
= \left( \frac{(1.2 \text{ atm})(6.022 \times 10^{23} \text{ mol}^{-1})}{(0.0821 \text{ L} \cdot \text{ atm} \cdot \text{ mol}^{-1} \cdot \text{ K}^{-1})(281 \text{ K})} \right)^{1/2} \sqrt{2} \left( 4.3 \times 10^{-19} \text{ m}^2 \right) \frac{8(8.314 \text{ J} \cdot \text{ mol}^{-1} \cdot \text{ K}^{-1})(281 \text{ K})}{\pi(0.0280 \text{ kg} \cdot \text{ mol}^{-1})}
\]

\[
z_{11} = 8.8 \times 10^9 \text{ s}^{-1}.
\]

b) What is the mean free path of \( \text{N}_2 \) at 1.2 atm and a gas density of 52.0 moles/m\(^3\)?

Mean free path:

\[
\lambda = \frac{1}{\sqrt{2} \alpha} \left( \frac{RT}{PN_A} \right) = \frac{1}{\sqrt{2} \left( 4.3 \times 10^{-19} \text{ m}^2 \right)} \left( \frac{0.0821 \text{ L} \cdot \text{ atm} \cdot \text{ mol}^{-1} \cdot \text{ K}^{-1})(281 \text{ K})}{(1.2 \text{ atm})(6.022 \times 10^{23} \text{ mol}^{-1})} \right) (\text{Im}^3/1000 \text{ L})
\]

\[
\lambda = 5.2 \times 10^{-8} \text{ m}
\]