Chemistry 4A, Fall 2017 **Name, Section #** Michael Li Babseem # 401 Hannah Kenagy
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Midterm 3

Potentially useful equations:

Gravitational potential energy: $E_g = mgh$; Kinetic energy: $KE = mv^2/2$

Density of gas: $\rho = \frac{MP}{RT}$; Result of kinetic theory of gases: $PV = \frac{1}{3}Nmv^2$

Mean free path of gas molecules: $\lambda = \frac{1}{\sqrt{2}n_V \pi d^2}$

Maxwell–Boltzmann distribution: $f(v) = 4\pi v^2 \left[\frac{M}{2\pi RT}\right]^{3/2} \exp\left[-\frac{1}{2}\frac{Mv^2}{RT}\right]$

Van der Waals equation: $\left[P + a\left(\frac{n}{V}\right)^2\right](V - nb) = nRT$; "Compressibility Factor": $z = \frac{PV}{nRT}$

Work in reversible isothermal processes: $w = -nRT\ln\frac{V_\infty}{V_1} = -nRT\ln\frac{P_1}{P_\infty}$

Molecular heat capacity of ideal monoatomic gases: $C_{V,m} = \frac{3}{2}R$; $C_{P,m} = \frac{5}{2}R$

Permutation of n different items: $n! = n(n-1)(n-2)\ldots1$

Combination: choosing L items from N items: ${}^{N}C_L = \frac{N!}{(N-L)!L!}$

Number of microstates for an ideal gas: $\Omega = gV^N U^{3N/2}$

Potentially useful constants:

$g = 9.8$ m/s^2; 1 atm ~101325 Pa ~760 mm Hg; 1 bar = 10^5 Pa

$R = 8.314$ J mol^{-1} K^{-1} = 0.08206 L atm mol^{-1} K^{-1}; 1 mol gas occupies 22.4 L at 0 °C

$k_B = 1.381 \times 10^{-23}$ m^2 kg s^{-2} K^{-1}

T(0 °C) = 273.15 K; 1 cal = 4.18 J

Density of liquids: ρ(Hg) = 13.6 g/mL; $\rho(H_2O)$ = 1.00 g/mL

Relative atomic mass: H=1, C=12, N=14, O=16, Cl =35.5

$N_A = 6.02\times10^{23}$

Full score of this exam is 100 points.

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<u>Part I. Multiple choices</u> (5 points each question; only <u>one</u> correct answer. Please circle correct answer)

1. Recall that the maximal range of lift for a suction pump at 1 atm is 10.3 m for water. The maximal range of lift at 1 atm for pumping petroleum (ρ = 0.80 g/mL) is (   )

   A. 10.3 m   B. 8.24 m   C. 12.9 m   D. 760 mm

2. In the van der Waals equation (Page 1), the factor *a* is introduced to correct for: (   )

   A. the volume occupied by the molecules themselves
   B. the effects of the kinetic energy of the molecules
   C. the momentum changes when molecules collide
   D. the effects of forces of attraction between molecules
   E. statistical variations resulting from the crooked paths traveled by molecules

3. Which of the statements below is true for a CO_2 fire extinguisher? (   )

   A. The gas temperature drops when operated in vacuum $P_{ext}=0$, $w=0$
   B. The gas temperature increases when operated in vacuum $w=0$
   C. The gas temperature drops when operated at 1 atm
   D. The gas temperature increases when operated at 1 atm
   E. May be used for putting out fire of magnesium

4. For below **<u>unbalanced</u>** reactions, which reaction has $\Delta U = \Delta H$? (   )

   A. $N_2O(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$ +1 $\Delta U - \Delta H = \Delta n_g RT$
   B. $C_{12}H_{22}O_{11}(s) + O_2(g) \rightarrow CO_2(g) + H_2O(l)$
   C. $C(s) + S(s) \rightarrow CS_2(g)$ +2
   D. $SO_2(g) + O_2(g) \rightarrow SO_3(g)$ −1

5. For an ideal gas system, which of the below is **<u>NOT</u>** a state function? (   )

   A. Internal energy *U*
   B. Heat *q*
   C. Enthalpy *H*
   D. Temperature *T*
   E. Entropy *S*

$\Delta T=0 \Rightarrow \Delta U=0$ so $q=-w$.

6. At 1 atm, an ideal gas system is expanded in volume through an isothermal process. We conclude: (   )

   A. The system absorbed heat from the surroundings. $\Delta V>0$ ∴ $w<0$
   B. The system released heat to the surroundings.
   C. There is no heat exchange between the system and the surroundings.   so $q>0$
   D. No conclusion can be drawn about the heat exchange between the system and the surroundings.

7. For 6 gas molecules in the two-chamber system discussed in class. What is the statistical probability for all molecules being in the left chamber? (   )

   A. 0   B. 1/720   C. 1/36   D. 1/64

$$\frac{1}{2^6} = \frac{1}{64}$$

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Part II. Questions. Short answers are fine as long as to the point.

For full credit please show your work and respond bellow each question. Work in the margins will not be graded.

Question 1. (6 points per question) Analysis: Are the following statements true or false? For each statement, first state unequivocally whether the statement is true or false (2 points). Afterwards, for statements you answer "true", discuss the mechanisms. For statements you answer "false", either discuss the mechanisms, or give one specific counter-example to disprove the statement. (4 points for the explanation)

(a) The velocity distribution of N_2 at a given temperature may be indistinguishable from that of O_2 at a different temperature.

True. MM=28

The velocity distribution of N_2 at T_1 is based on the factors M and T which are constants. Because O_2 has a higher (MM=32) molar mass, it has a smaller velocity average and may imply that a skinnier distribution. But, the O_2 is at a different temperature and may imply that there just has to be one possibility. Thus, if T_2 or T_{O_2} is higher than $T_1 = T_{N_2}$ then an increase in temperature would increase the v_{avg} distribution and broaden the curve. This would effect and counteract the increase in molar mass. Looking at the equation, the f(v) is dependent on $\frac{M}{T}$. Thus if $\frac{M_1}{T_1} = \frac{M_2}{T_2}$ then the velocity distributions will be indistinguishable

$f(v) = 4\pi v^2 \left[\frac{M}{2\pi RT}\right]^{3/2} e^{\dots}$ so f(v) is dependent on $\frac{M}{T}$ ... $\frac{M_1}{T_1} = \frac{M_2}{T_2}$ ... for $T_1 \neq T_2$ so $f(v)$ ... contained to $f(v)_{O_2}$ ...

(b) For an ideal gas that does not go through any chemical reactions, $\Delta H = 0$ for all isothermal processes.

~~For~~ False.

Because ΔU is only dependent on ΔT

$\Delta H = \Delta(U+PV) = \Delta U + \Delta(PV)$ which for an isothermal process = 0, then

$\Delta U = 0$ but $\Delta H = \Delta(PV)$. Gas can still expand or compress isothermally so ΔH does not have to be 0 as $\Delta(PV)$ for expansions and compressions $\neq 0$ if it's expanding. One counterexample is if it is expanding against a constant pressure then, $\Delta H = \Delta(PV) = \boxed{+P_{ext}\Delta V}$

(c) The standard enthalpy of formation is 0 for any pure element.

False.

For the pure element Br, the enthalpy of formation will be $\neq 0$. This is because the ΔH_f° is based on the most stable form of the element at 1atm and a given temp (usually 25°C). The most ~~common~~ stable form of Bromine at 1atm @25°C is $Br_2(l)$. ~~Thus~~ The Br in this case, the pure element Br, has a higher ΔH_f° because ~~be~~ the Br atoms are less stable than the bond that is formed between Br_2. Thus, because Br is less stable ΔH_f°, which is based on ΔU will be greater as its internal energy is greater so $\Delta H_f^\circ \neq 0$ and the statement is false.

(d) Number of microstates, Ω, is an extensive function that depends linearly on system size.

False

Ω is a function of U, V, N and has the form $\Omega(U,V,N) = gV^N U^{3N/2}$.

If it did depend linearly on size than $\Omega(2V)$ would be equal to $2\Omega(V)$

so it would assume that $\frac{\Omega(2V)}{\Omega(V)} = 2$ But $\frac{\Omega(2V)}{\Omega(V)} = \frac{g(2V)^N U^{3N/2}}{gV^N U^{3N/2}} = \left(\frac{2V}{V}\right)^N = 2^N$ which is a huge increase in Ω and, $2^N \neq 2$ for $N \neq 1$ so the statement that Ω is a linear function that depends linearly on system size is false

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Question 2. (8 Points) A glass vessel weighted 40 g when pumped to vacuum, 40.14 g when filled with N_2 at 1 atm, and 40.30 g when filled with an unknown gas X at 1 atm. What is the molecular weight of gas X?

$40.14 - 40 = m_{N_2}$

constant

$$\frac{\frac{m_{N_2}}{MM_{N_2}} \cdot \cancel{RT}}{P_n} = \frac{n_2 \cancel{RT}}{P_2} \quad \text{so} \quad \frac{m_{N_2}}{MM_{N_2} P_{N_2}} = \frac{m_x}{MM_x \cdot P_x} \Rightarrow$$

$$\Rightarrow MM_x = \frac{m_x \, P_{N_2} MM_{N_2}}{m_{N_2} \, P_x} = \frac{(40.30 - 40) \cdot 1\,atm \cdot 28\,g/mol}{(40.14 - 40) \cdot 1\,atm}$$

$$= MM_x = 60 = \boxed{60\,g/mol}$$

Question 3. (8 Points) Given that the internal energy of a monoatomic ideal gas system is $U = 3/2\ nRT$, calculate the root-mean-square (RMS) velocity of N_2 molecules in this room (assume $T = 300$ K). Explain why the actual diffusion speeds of molecules are much slower than this value.

$$U = KE = \frac{3}{2} nRT = \frac{1}{2} N m \cdot \overline{v^2}$$

$$\sqrt{\overline{v^2}} = \sqrt{3RT \cdot \frac{n}{Nm}} \qquad \frac{n}{Nm} = \text{Molar mass} = M$$

$$\text{so } \sqrt{\overline{v^2}} = V_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \cdot 8.3145 \cdot 300}{28\,g/mol \cdot \frac{1\,kg}{1000\,g}}}$$

$$V_{rms, N_2} = 516.96 = 520\ m/s$$

Actual diffusion speeds are alot lower than this because in a given container of N_2, there are alot of collisions which change the velocity of the molecules, thus, because the velocity changes so often the Δx or the change of its position is not $= \Delta V \cdot t$ and the ~~...~~ V_{avg} ... will be smaller than the V_{rms}. the mean free path ~100 nm so the ~~...~~ atoms can change direction every ~100 nm really to a path example like

$\Delta x / \Delta t$ ↳ not representative of V_{rms}.

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Question 4. (10 Points) Octane (C_8H_{18}) is a major component of gasoline. Its combustion can be written as:

$$2\,C_8H_{18}(l) + 25\,O_2(g) \longrightarrow 16\,CO_2(g) + 18\,H_2O(l)$$

(a) (6 points) At 0 °C, what **volume** of ***air*** is needed to burn 1 mol octane? Assume that the partial pressure of O_2 in the air is 0.20 atm. Keep two significant figures for the final result.

$1\text{ mol Octane} \cdot \dfrac{25\text{ mole } O_2}{2\text{ mole } C_8H_{18}} = 12.5\text{ mole } O_2$ $\quad P_{O_2} = X_{O_2} \cdot P_{air}$ $\quad \dfrac{P_{O_2}}{X_{O_2}} = P_{air}$

$V_{O_2} = \dfrac{nRT}{P} = \dfrac{12.5 \cdot 0.08206 \cdot (0+273)}{0.2} = \cancel{1400\,L} = V_{O_2} = \boxed{1400\,L}$

$V_{O_2} = V_{air}$

assumption is that tussut lation air or STP so $P_{air} = 1\text{ atm}$, $P_{O_2} = 0.2\text{ atm}$, $X_{O_2} = \dfrac{P_{O_2}}{P_{air}} = \dfrac{0.2}{1} = 0.2$

$\dfrac{1400}{0.2} = 7009.74\,L\text{ air} = \boxed{7.0 \times 10^3\,L\text{ air}}$

(b) (4 points) Given $\Delta_f H^\circ[C_8H_{18}(l)] = -250\text{ kJ/mol}$, $\Delta_f H^\circ[H_2O(l)] = -286\text{ kJ/mol}$, $\Delta_f H^\circ[CO_2(g)] = -394\text{ kJ/mol}$, calculate $\Delta_f H^\circ$ of the reaction.

$= 18(\Delta_f H^\circ[H_2O(l)]) + 16(\Delta_f H^\circ[CO_2(g)]) - 25(0) - 2(\Delta_f H^\circ[C_8H_{18}(l)])$

$18 \cdot -286 + 16 \cdot -394 \quad -0 - 2(-250) = -10{,}952$

$\boxed{-11{,}000\text{ kJ/mol}} = \Delta_f H^\circ_{rxn}$

Question 5. (15 Points) Storage and transport of energy is a challenge of modern society. What is the amount of water that is needed to store 2.0×10^6 J energy in the following ways? You may refer to formulas and values on the first page. **Give answers in kg**.

(a) (5 points) Store the energy as gravitational potential energy by elevating *x* kg of water to a height of 10 m.

$|q| = |w| \Rightarrow w = mgh = x\text{ kg} \cdot 9.8 \cdot 10\text{ m} = 2.0 \times 10^6$

$x\text{ kg} = 20408\text{ kg}$

$x = \boxed{2.0 \times 10^4\text{ kg}}$

(b) (5 points) Store the energy by heating up *x* kg of water from room temperature (25 ˚C) to 50 ˚C.

$$q = mC\Delta t$$

$$q = 2.0\times10^{6}J = X kg \cdot \frac{1000g}{1kg} \cdot (4.18J/g\cdot1°C) \cdot (80°C - 25°C)$$

$$X = 191.392\ kg = \boxed{190\ kg\ H_2O}$$

(c) (5 points) Store the energy by splitting *x* kg of water into H_2 and O_2 at 1 atm. $\Delta_f H^\circ(H_2O) = -286$ kJ/mol.

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \quad \Delta_f H^\circ(H_2O) = -286 kJ/mol$$

$\Delta H_f^\circ\ H_2O \rightarrow H_2 + \tfrac{1}{2}O_2$ for the reverse reaction

$\Delta H = q$

$$\Delta H^\circ = -\Delta_f H^\circ(H_2O) \quad (+286)\ kJ/mol \cdot \frac{1 mol}{18g\ H_2O}\left(X kg\left(\frac{1000g}{1kg}\right)\right) = 2.0\times10^{6} J$$

$= 286 \frac{kJ}{mol}$ $\cdot \frac{1000J}{1kJ}$

$$\Delta H = q \qquad X kg = 0.1258 = \boxed{0.12\ kg\ H_2O} = x.$$