## NAME: ACETONE

Score: /10
[Show all work clearly. All numbers without decimals may be assumed to be infinitely precise. Be sure to show proper units in every case.]

1. (5 points) Draw structures for the following molecules to the right of each name.
P-Aminobenzoic acid
2. ( $\mathbf{5}$ points) In the table, indicate the proper best definition of each word or phrase in column $A$ by inserting the proper number from column B :

| Column A | Column B |
| :---: | :---: |
| __9__ Equilibrium | 1. A property proportional to the "size" of the system |
| __3__ Gas constant | 2. A property independent of the "size" of the system |
| __2__ Intensive property | 3. Fundamental constant of the universe, given as $8.3144349 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$ in Sl units |
| __6__ Surroundings | 4. Describing a macroscopic system in which the parts are observed to exchange energy over time |
| __8__ Heat capacity | 5. Statement of the zeroth law of thermodynamics |
|  | 6. Everything in the universe except the system under study |
|  | 7. Describing a multi-part system in which the parts exchange thermal energy through their boundaries |
|  | 8. Measure of the amount of energy required to change the temperature of a substance by a given amount |
|  | 9. The condition of a system for which no macroscopic change is observed |

## NAME: ACETONE

Score: _/10
3. (10 points) For each entry on the left, given the derivative with respect to the independent variable indicated. (A, B, C, and n are constants.)

| Function |  |
| :---: | :---: |
| $f(T)=e^{-A / T^{2}}$ | $\frac{d f}{d T}=\frac{2 A}{T^{3}} e^{-A / T^{2}}$ |
| $g(E)=A+B E^{2}+\frac{C}{E}$ | $\frac{d g}{d E}=2 B E-\frac{C}{E^{2}}$ |
| $P V=n R T$ | $\left(\frac{\partial P}{\partial T}\right)_{V}=\frac{n R}{V}$ |
| $f(T)=e^{-A / T^{2}}$ | $\frac{d}{d T} \ln f=\frac{2 A}{T^{3}}$ |
| $h(x)=\frac{A}{B-C x}$ | $\frac{d h}{d x}=\frac{A C}{(B-C x)^{2}}$ |

NAME: BIPHENYL
Score:_____/20
[Show all work clearly. Be sure to show proper units and correct number of significant figures.]

1. (5 points) In Table 4.1 in the Handbook, the van der Waals parameter, a , for $\mathrm{H}_{2} \mathrm{O}$ is about 150 times larger than the value of a for He. In one complete sentence, explain what this means about these two molecules.
The intermolecular attraction between water molecules is much stronger than the intermolecular interaction between helium atoms.
2. (5 points) In the box, indicate the correct definition (from column B) of the words or phrases in column A.

| Column A | Column B |
| :---: | :---: |
| e_ Elastic collision | a. Absolute temperature |
| f Mole fraction of substance i | b. Boltzmann's constant |
| d_- Pressure | c. Celsius |
| a Thermodynamic temperature scale | d. Force per unit area |
| g__ Zeroth Law | e. No change in translational energy |
|  | f. $\mathrm{P}_{\mathrm{i}} / \mathrm{P}_{\text {total }}$ |
|  | g. Two systems in thermal equilibrium with a third system at temperature T are also in thermal equilibrium with each other. |

3. (10 points) An athlete at high performance may inhale 3.75 liters of air at 1.00 atm and 298.15 K . The inhaled air contains $0.5 \%$ water by volume and the exhaled air contains $6.2 \%$ by volume. For a respiration rate of 32 breaths per minute, how many moles of water are exhaled per minute through the lungs?

First, calculate the volume expelled per breath: $\Delta V=(0.062-0.005)(3.75 L)=0.21375 \mathrm{~L}$ In 32 breaths, the expelled volume is: $\Delta V_{\text {total }}=32(0.21375 \mathrm{~L})=6.84 \mathrm{~L}=6.84 \times 10^{-3} \mathrm{~m}^{3}$ This volume corresponds to a specific number of moles:
$\Delta n=\frac{P \Delta V_{\text {total }}}{R T}=\frac{(101325 \mathrm{~Pa})\left(6.84 \times 10^{-3} \mathrm{~m}^{3}\right)}{\left(8.3144349 \mathrm{~J} \mathrm{~K}^{-1}\right)(298.15 \mathrm{~K})}=0.280 \mathrm{~mole}$

NAME: CARBON TETRACHLORIDE
Score: /20
[Show all work clearly. All numbers without decimals may be assumed to be infinitely precise. Be sure to show proper units in every case.]

1. (6 points) Using van der Waals constants, estimate the radius of a methane molecule, assuming that the molecule is a sphere.
The van der Waals $b$ for methane is $43.0637 \times 10^{-6} \mathrm{~m}^{3} / \mathrm{mol}$. The excluded volume per molecule is therefore $V_{\text {molecule }}=\frac{b}{N_{0}}=\frac{43.0637 \times 10^{-6} \mathrm{~m}^{3} / \mathrm{mol}}{6.02211415 \times 10^{23} \mathrm{molecule} / \mathrm{mol}}=7.15093 \times 10^{-29} \mathrm{~m}^{3} / \mathrm{molecule}$. This is the point where two molecules just touch, so $V_{\text {molecule }}=(2 r)^{3}$, where $r$ is the radius of the molecule. Solving for the radius gives the "size" of the methane molecule:

$$
r=\sqrt[3]{\frac{V_{\text {molecule }}}{8}}=\sqrt[3]{\frac{\left(7.15093 \times 10^{-29} \mathrm{~m}^{3}\right)}{8}}=2.07535 \times 10^{-10} \mathrm{~m}
$$

One may also use this equation, which is in the book:

$$
\sigma=\sqrt[3]{\frac{3 b}{2 \pi N_{0}}}=\sqrt[3]{\frac{3\left(43 / 0637 \times 10^{-6} \mathrm{~m}^{3} / \mathrm{mol}\right)}{2 \pi\left(6.02211415 \times 10^{23} \mathrm{molecule} / \mathrm{mol}\right)}}=3.24415 \times 10^{-10} \mathrm{~m}
$$

From this, one finds $r=1.62208 \times 10^{-10} \mathrm{~m}$. Either method is counted correct.
2. (4 points) The one-dimensional speed distribution function is $f\left(v_{x}\right)=\sqrt{\frac{2 m}{\pi k T}} \exp \left(-\frac{m v_{x}^{2}}{2 k T}\right)$, where the symbols have their usual meaning. Derive an equation for the average speed, $\left.<v_{x}\right\rangle$ in one dimension.

One merely does the integral: $\left\langle v_{x}\right\rangle=\int_{0}^{\infty} f\left(v_{x}\right) v_{x} d v_{x}=\sqrt{\frac{2 m}{\pi k T}} \int_{0}^{\infty} v_{x} \exp \left(-\frac{m v_{x}^{2}}{2 k T}\right) d v_{x}=\sqrt{\frac{2 k T}{\pi m}}$
3. (10 points) In the following, indicate which statements match the word or phrase in column A the best by putting the letter of it in the blank next to the answer. [There is only one best answer for each.]

| Column A | Column B |
| :--- | :--- |
| ___ Boyle temperature | a. $A \exp \left(-\frac{E}{k T}\right)$ |
| _e__ Compression factor | b. $B \exp \left(-\frac{x^{2}}{2 \sigma^{2}}\right)$ |
| _d_ Critical temperature | C. For a van der Waals gas, $\frac{a}{R b}$ |
| _b_ Gaussian | d. Condition at which $\left(\frac{\partial P}{\partial V_{m}}\right)_{T}=0$ and $\left(\frac{\partial^{2} P}{\partial V_{m}^{2}}\right)_{T}=0$ |
| _a_B Boltzmann factor | e. $\frac{P V_{m}}{R T}$ |

NAME: DIOXANE
Score: $\qquad$
[Show all work clearly. All numbers without decimals may be assumed to be infinitely precise. Be sure to show proper units in every case.]

1. (6 points) Suppose you draw a single card from a standard 52-card deck. (a) What is the probability of drawing an ace of any suit?

There are four aces out of 52 cards, so the probability is $P=\frac{4}{52}=0.07692$
(b) What is the probability of drawing the ace of hearts from a standard deck?

There is only one ace of hearts, so the probability is $P=\frac{1}{52}=0.01923$
2. (6 points) Determine the rms speed of Kr at 298.15 K .

$$
u=\sqrt{\frac{3 k T}{m}}=\sqrt{\frac{3 R T}{M}}=\sqrt{\frac{3\left(8.3144349 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}\right)(298.15 \mathrm{~K})}{0.083798 \mathrm{~kg} \mathrm{~mol}^{-1}}}=297.90 \mathrm{~m} \mathrm{~s}^{-1}
$$

3. (4 points) For a particular system, the internal energy is given by the following equation:
$U(T, V)=U_{0}+A T+B V$, where $U_{0}, A$, and $B$ are constants independent of temperature and volume. Show that this is a mathematically acceptable form for $U$ as a state function. [Show all work; explain.] One has to show the Maxwell relation: $\left(\frac{\partial U}{\partial T}\right)_{v}=\left(\frac{\partial}{\partial T}\left(U_{0}+A T+B V\right)\right)_{v}=A$ and $\left(\frac{\partial U}{\partial V}\right)_{T}=$ $\left(\frac{\partial}{\partial V}\left(U_{0}+A T+B V\right)\right)_{T}=B . \operatorname{But}\left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_{V}\right)_{T}=\left(\frac{\partial A}{\partial V}\right)_{T}=0$. Similarly $\left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_{T}\right)_{V}=\left(\frac{\partial B}{\partial T}\right)_{V}=$ 0 . These two crossed partial derivatives are equal, which is the requirement for an acceptable state function.
4. (4 points) Helium gas is expanded from a molar volume of 22.4 liters to a molar volume of 44.8 liters against a constant external pressure of 0.500 bar. How much work does the amount of gas do in this process?
The work done by the gas is

$$
w=P_{\text {ext }}\left(V_{2}-V_{1}\right)=0.500 \times 10^{5} \mathrm{~Pa}\left(44.8 \times 10^{-3} \mathrm{~m}^{3}-22.4 \times 10^{-3} \mathrm{~m}^{3}\right)=1.12 \mathrm{~kJ}
$$

NAME:
FURAN
Score: 120
[Show all work clearly. All numbers without decimals may be assumed to be infinitely precise. Be sure to show proper units in every case.]

1. ( 12 points) Calculate the change in enthalpy of water when it is heated from room temperature (298.15 K) to its normal boiling point (373.15 K), as accurately as you can.

$$
\begin{aligned}
\Delta H_{m}= & \int_{298.15 K}^{373.15 K} C_{P m} d t \\
& =\int_{298.15 K}^{373.17 K}\left(-203.6060+1.523290 T-0.003196413 T^{2}+2.474455 \times 10^{-6} T^{3}\right. \\
& \left.+\frac{3.855326 \times 10^{6}}{T^{2}}\right) d T J \\
& =\left(-203.6060 T+\frac{1.523290}{2} T^{2}-\frac{0.003196413}{3} T^{3}+\frac{2.474455 \times 10^{-6}}{4} T^{4}\right. \\
& \left.-3.855326 \times 10^{6}\left(\frac{1}{T}\right)\right)_{298.15 K}^{373.15 K} J \\
& =\left(-203.6060(373.15-298.15)+\frac{1.523290}{2}\left(373.15^{2}-298.15^{2}\right)\right. \\
& -\frac{0.003196413}{3}\left(373.15^{3}-298.15^{3}\right)+\frac{2.474455 \times 10^{-6}\left(373.15^{4}-298.15^{4}\right)}{4} \\
& \left.-3.855326 \times 10^{6}\left(\frac{1}{373.15}-\frac{1}{298.15}\right)\right) \mathrm{J} \\
& =-15,270.45 \mathrm{~J}+38,346.92 \mathrm{~J}-27,120.69 \mathrm{~J}+7,105.39 \mathrm{~J}+2,598.99 \mathrm{~J}=5,660.16 \mathrm{~J}
\end{aligned}
$$

But this is on a molar basis. The molar mass of water is 18.00994 gm , so one can find this on a weight basis by division:

$$
\Delta H=\frac{5,660.16 \mathrm{~J}}{18.00994 \mathrm{gm}}=314.28 \mathrm{~J} \mathrm{gm}^{-1}
$$

2. (8 points) For a gas that obeys the van der Waals equation of state, determine $\left(\frac{\partial P}{\partial T}\right)_{V_{m}}$ as a function of $T, V_{m}$, and the van der Waals constants.

For a van der Waals gas, $P=\frac{R T}{V_{m}-b}-\frac{a}{V_{m}^{2}}$. Taking the derivative of this function gives

$$
\left(\frac{\partial P}{\partial T}\right)_{V_{m}}=\left(\frac{\partial}{\partial T}\left(\frac{R T}{V_{m}-b}\right)\right)_{V_{m}}-\left(\frac{\partial}{\partial T} \frac{a}{V_{m}^{2}}\right)_{V_{m}}=\frac{R}{V_{m}-b}-0=\frac{R}{V_{m}-b}
$$

## NAME:

GLYCOSIDE
Score: /20
[Show all work clearly. All numbers without decimals may be assumed to be infinitely precise. Be sure to show proper units in every case.]

1. (10 points) Assume that you have an ideal gas with a temperature-independent heat capacity, $C_{V m}=\frac{5}{2} R$. (a) Suppose that you carry 2.60 moles of this gas through a reversible expansion that doubles the volume at constant temperature. What is the change in entropy?

$$
\begin{gathered}
\Delta S=\int_{V_{1}}^{V_{2}}\left(\frac{\partial S}{\partial V}\right)_{T} d V=\int_{V_{1}}^{V_{2}}\left(\frac{\partial P}{\partial T}\right)_{V} d V=n R \int_{V_{1}}^{2 V_{1}} \frac{1}{V} d V=n R \ln \left(\frac{2 V_{1}}{V_{1}}\right) \\
=(2.60)\left(8.3144349 \mathrm{JK}^{-1}\right) \ln (2)=14.98 \mathrm{JK}^{-1}
\end{gathered}
$$

(b) Suppose that you carry the same amount of this gas through a process in which the temperature goes from the starting temperature of 298.15 K to 398.15 K , while holding the volume constant. What is the entropy change during that process?

$$
\begin{gathered}
\Delta S=\int_{T_{1}}^{T}\left(\frac{\partial S}{\partial T}\right)_{V} d T=\int_{298.15 K}^{398.15 K} \frac{C_{V}}{T} d T=n\left(\frac{5 R}{2}\right) \ln \left(\frac{398.15 K}{298.15 K}\right) \\
=(2.60)\left(\frac{5 * 8.3144349 \mathrm{JK}^{-1}}{2}\right) \ln (1.33540) \\
=15.63 \mathrm{JK}^{-1}
\end{gathered}
$$

2. (10 points) Which of the following equations is/ are correct, and which is/ are incorrect? Mark an $X$ in the appropriate box. (Graded right - 0.5 wrong ; do not guess.)

| EQUATION | Correct | Incorrect |
| :--- | :---: | :---: |
| $\left(\frac{\partial H^{\theta}}{\partial T}\right)_{P}=C_{P}^{\theta}$ | X |  |
| $\left(\frac{\partial S^{\theta}}{\partial P}\right)_{T}=\left(\frac{\partial V^{\theta}}{\partial T}\right)_{P}$ |  | X |
| $\left(\frac{\partial S^{\theta}}{\partial T}\right)_{P}=\frac{C_{V}^{\theta}}{T}$ | X |  |
| $d S=\left(\frac{\partial S}{\partial T}\right)_{P} d T+\left(\frac{\partial S}{\partial V}\right)_{T} d V$ | X | X |
| $H(T, P)=H^{\theta}(T)+\int_{P^{\theta}}^{P}\left(V-T\left(\frac{\partial V}{\partial T}\right)_{P}\right) d P$ |  |  |

[Show all work clearly. All numbers without decimals may be assumed to be infinitely precise. Be sure to show proper units in every case.]

1. (8 points) Using information in the Handbook, calculate the molar entropy of fusion of water at its normal melting point.

From the Handbook's Table 6.1, the information is: $T_{f}=273.15 \mathrm{~K}$ and $\Delta H_{f, m}^{\theta}=6.01 \mathrm{~kJ} \mathrm{~mol}^{-1}$
By definition $\Delta S_{f, m}^{\theta}=\frac{\Delta H_{f, m}^{\theta}}{T_{f}}=\frac{6.01 \times 10^{3} \mathrm{Jmol}^{-1}}{273.15 \mathrm{~K}}=22.0 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$
2. (8 points) Consider a reversible Carnot engine using an ideal gas that operates between room temperature (298.15 K) and 498.15 K. (a) If one extracts exactly 1 kJ of heat at 498.15 K , how much work can the engine do?
First calculate the ideal efficiency: $\varepsilon=\frac{T_{\text {hot }}-T_{\text {cold }}}{T_{\text {hot }}}=\frac{498.1 \mathrm{~K}-298.15 \mathrm{~K}}{498.15 \mathrm{~K}}=0.4015$
That determines how much of the heat is used as work: $w=\varepsilon q=(0.40125)(1 \mathrm{~kJ})=401.25 \mathrm{~J}$
(b) Secondly, consider a Carnot engine working between the same temperatures as in (a), except that it uses a van der Waals gas as the working fluid. What is the maximum work one can achieve from this engine for an input of exactly 1 kJ ?

The ideal efficiency gives maximum work, so the maximum work is the same: 401.25 J
3. (4 points) In each case, give the simplest requirement for spontaneity in terms of an inequality.

| Constant temperature and constant volume | $(\Delta A)_{T, V} \leq 0$ |
| :--- | :---: |
| Constant temperature and constant pressure | $(\Delta G)_{T, P} \leq 0$ |

NAME:
INDIGO
Score: $\qquad$ /20
[Show all work clearly. All numbers without decimals may be assumed to be infinitely precise. Be sure to show proper units in every case.]

1. (10 points) (a) Using data in your handbook, calculate the enthalpy of the dissociation of bromine at 298.15 K by the reaction

$$
B r_{2}(g) \rightarrow 2 B r(g)
$$

This is done using data for the various formation enthalpies in Table 5.8.

$$
\Delta H^{\theta}=2 \Delta_{f} H_{m}^{\theta}(B r)-\Delta_{f} H_{m}^{\theta}\left(B r_{2}\right)=2(111.9 \mathrm{~kJ})-30.9 \mathrm{~kJ}=193.8 \mathrm{~kJ}
$$

(b) Also using data from your handbook, calculate the Gibbs free energy change for the same reaction at 298.15 K .

From the same data table, one can find the Gibbs energy change in an analogous manner:

$$
\Delta G^{\theta}=2 \Delta_{f} G_{m}^{\theta}(B r)-\Delta_{f} G_{m}^{\theta}\left(B r_{2}\right)=2(82.4 \mathrm{~kJ})-3.1 \mathrm{~kJ}=161.7 \mathrm{~kJ}
$$

2. (10 points) Calculate the change in entropy when one mole of water is heated from 298.15 K to 308.15 K at a constant pressure of 1 bar.

This calculation involves only a change in temperature so the change is calculated as follows:

$$
\Delta S_{m}^{\theta}=\int_{298.15 K}^{308.15 K}\left(\frac{\partial S_{m}^{\theta}}{\partial T}\right)_{P} d T=\int_{298.15 K}^{308.5 K} \frac{C_{P m}^{\theta}(T)}{T} d T
$$

Substitution from Table 5.6 for the temperature-dependent heat capacity gives:

$$
\begin{aligned}
& \Delta S_{m}^{\theta}=\int_{298.15 K}^{308.5 K} \frac{c_{1}+c_{2} T+c_{3} T^{2}+c_{4} T^{3}+c_{5} T^{-2}}{T} d T=\int_{T_{1}}^{T_{2}}\left(\frac{c_{1}}{T}+c_{2}+c_{3} T+c_{4} T^{2}+\frac{c_{5}}{T^{3}}\right) d T \\
&=c_{1} \ln \left(\frac{T_{2}}{T_{1}}\right)+c_{2}\left(T_{2}-T_{1}\right)+\frac{c_{3}}{2}\left(T_{2}^{2}-T_{1}^{2}\right)+\frac{c_{4}}{3}\left(T_{2}^{3}-T_{1}^{3}\right)-\frac{c_{5}}{2}\left(\frac{1}{T_{2}^{2}}-\frac{1}{T_{1}^{2}}\right) \\
&=\left[(-203.6060) \ln \left(\frac{308.15}{298.15}\right)+1.523290(308.15-298.15)\right. \\
&-\frac{3.196413 \times 10^{-3}}{2}\left(308.15^{2}-298.15^{2}\right)+\frac{2.474455 \times 10^{-6}}{3}\left(308.15^{3}-298.15^{3}\right) \\
&\left.-\frac{3.855326 \times 10^{6}}{2}\left(\frac{1}{308.15^{2}}-\frac{1}{298.15^{2}}\right)\right] \frac{J}{K(\mathrm{~mol})} \\
&=[-6.7170+15.2329-9.6899+2.2742+1.3846] \frac{J}{K(\mathrm{~mol})}=2.4848 \frac{\mathrm{~J}}{K(\mathrm{~mol})}
\end{aligned}
$$

Note that using a temperature-independent $C_{p m}$ in the simple equation gives a similar value, but the correct way of working the problem is to include all temperature-dependent terms. Using a temperature-independent heat capacity without explicitly saying why you assume temperature independence (in this case, because the temperature range is small) shows a lack of knowledge of the general usage of these equations.

NAME:
KERATIN
Score: /20
[Show all work clearly. All numbers without decimals may be assumed to be infinitely precise. Be sure to show proper units in every case.]

1. (10 points) A commonly studied reaction is the dimerization of $\mathrm{NO}_{2}$ to dinitrogen tetroxide in the gas phase:

$$
2 \mathrm{NO}_{2}(\mathrm{~g}) \quad \rightarrow \quad \mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g})
$$

(a) Predict, by calculation, the equilibrium constant for this reaction at 298.15 K . [Show all work.]

First method from free energies of formation: $\Delta G^{\theta}=99.8 \mathrm{~kJ}-2(51.3 \mathrm{~kJ})=-2.8 \mathrm{~kJ} \Rightarrow$

$$
K_{a}(298.15 K)=\exp \left(-\frac{-2800 \mathrm{~J}}{8.3144349 \frac{J}{K}(298.15 \mathrm{~K})}\right)=3.09
$$

Second method from enthalpies of formation and Third-Law entropies: $\Delta G^{\theta}=\Delta H^{\theta}-T \Delta S^{\theta}=$ $(11.1 \mathrm{~kJ}-2(33.2 \mathrm{~kJ}))-(298.15 \mathrm{~K})\left(304.4 \frac{\mathrm{~J}}{\mathrm{~K}}-2\left(240.1 \frac{\mathrm{~J}}{\mathrm{~K}}\right)\right)=-55.3 \mathrm{~kJ}+52.4 \mathrm{~kJ}=$ $-2.9 \mathrm{~kJ} \Rightarrow K_{a}(298.15 K)=\exp \left(-\frac{-2900 J}{8.3144349 \frac{J}{K}(298.15 K)}\right)=3.22$, essentially the same number. Either method is considered correct.
(b) Assume that the pressures are sufficiently low that each component can be considered an ideal gas. Write a correct expression for $\mathrm{K}_{\mathrm{a}}$ in terms of the partial pressure of each gas, $\mathrm{P}_{\mathrm{i}}$, and any other necessary parameters. [Define any symbols you use.]

$$
K_{a}=\frac{P_{N_{2} O_{4}}}{P_{N O_{2}}^{2}} P^{\theta}
$$

where $P^{\theta}$ is the standard pressure (in the case of data from Table 5.8, that is 1 bar).
2. (10 points) Consider the dimerization of $\mathrm{NO}_{2}$, as discussed in question 1. Assume that for practical purposes, both $\Delta \mathrm{H}^{\theta}$ and $\Delta \mathrm{S}^{\theta}$ are temperature-independent. [This is an approximation, of course, and will lead to some errors, but may not be too bad.] Predict Ka for this reaction at 373.15 K , considering that approximation to be correct. [Show all work, including derivation of any intermediate quantities.]

In this case, one may use the second method, as in question 1, because the enthalpy and entropy changes are independent of temperature:

$$
\Delta G^{\theta}=\Delta H^{\theta}-T \Delta S^{\theta}=-55.3 \mathrm{~kJ}-(373.15 \mathrm{~K})\left(-175.8 \frac{\mathrm{~J}}{\mathrm{~K}}\right)=10.30 \mathrm{~kJ}
$$

And

$$
K_{a}(T)=\exp \left(-\frac{\Delta G^{\theta}}{R T}\right) \Rightarrow K_{a}(373.15 K)=\exp \left(-\frac{10300 \mathrm{~J}}{\frac{8.3144349 \mathrm{~J}}{K}(373.15 \mathrm{~K})}\right)=0.0362
$$

## NAME:

LYSERGIC ACID
Score: $\qquad$ /20
[Show all work clearly. All numbers without decimals may be assumed to be infinitely precise. Be sure to show proper units in every case.]

1. (10 points) Ratcliffe and Chao (Canad. J. Chem. Eng. 1969, 47, 148.) measured the properties of solutions of isopropanol ( $P_{1}^{\bullet}=1008$ torr ) and n-decane ( $P_{2}^{\bullet}=48.3$ torr ). For a particular solution, the liquid had a mole fraction, $X_{2}$, of 0.2040 and the total pressure over the solution, $P_{\text {total }}$, was 909.6 torr. They condensed the gas phase and measured that in gas, the n-decane gas-phase mole fraction was 0.0300 . From these data, find the activities, $a_{i}$, and activity coefficients, $\gamma_{i}$, of isopropanol and n-decane, assuming a Raoult's law standard state.

First calculate the partial pressures of the two components:

$$
P_{1}=Y_{1} P_{\text {total }}=0.9700(909.6 \text { torr })=882.3 \text { torr } \quad \text { and } \quad P_{2}=Y_{2} P_{\text {total }}=0.0300(909.6 \text { torr })=
$$ 27.3 torr. The activity on the Raoult's Law scale is $a_{i}=P_{i} / P_{i}^{\bullet}$. Using the values in the problem, this formula gives: $a_{\text {isopropanol }}=0.875$ and $a_{\text {decane }}=0.565$

At equilibrium, the activity of a component in the gas phase is equal to the activity in the liquid. So, we can calculate the activity coefficients from $a_{i}=\gamma_{i} X_{i}$. When one does that, the results are

$$
\gamma_{\text {isopropanol }}=a_{\text {isopropanol }} / X_{\text {isopropanol }}=0.875 / 0.796=1.10
$$

and

$$
\gamma_{\text {decane }}=a_{\text {decane }} / X_{\text {decane }}=0.565 / 0.2040=2.77
$$

2. (10 points) Below is a boiling point diagram for a solution of two materials, $A$ and $B$. The abscissa is the mole fraction of component $B$. Insert the appropriate letter(s) in the blank space(s) next to phrases to indicate the appropriate region(s) or point(s) which those phrases describe.

_(f) Boiling temperature of $B$
_(e)_Boiling temperature of $A$
_(g)__ Azeotrope
_(b)__ Liquid
(c)(d)_ Liquid + vapor
_(a)__ Vapor
Mole Fraction of B

NAME: MALEIC ANHYDRIDE
Score: /20
[Show all work clearly. All numbers without decimals may be assumed to be infinitely precise. Be sure to show proper units in every case.]

1. (10 points) An aqueous solution containing calcium chloride freezes at $-4^{\circ} \mathrm{C}$. If you were to heat this solution until it boils, what would the temperature be?

From Tables 7.5 and 7.6 in the Handbook, one finds $K_{b}=0.512 \mathrm{~K} \mathrm{~kg} / \mathrm{mol}$ and $K_{f}=1.860 \mathrm{~K} \mathrm{~kg} / \mathrm{mol}$. Since the molality is constant in the two processes:

$$
m=\frac{\theta_{b}}{K_{b}}=\frac{\theta_{f}}{K_{f}}
$$

Hence, $\theta_{b}=\frac{K_{b}}{K_{f}} \theta_{f}=\frac{0.512}{1.860}(4 \mathrm{~K})=1.101 \mathrm{~K}$.
Normally, water boils at $100^{\circ} \mathrm{C}$, so this solution boils at $101.01^{\circ} \mathrm{C}$.
2. (10 points) The Henry's Law constant for $N_{2}$ in water is $9.04 \times 10^{4}$ bar at 298.15 K , on the mole fraction scale. At equilibrium at this temperature, how many moles of $\mathrm{N}_{2}$ are dissolved in 1 kg of water with a nitrogen overpressure of 0.79 bar?

Because the solution is in the dilute limit, one may assume the activity coefficient is 1. Therefore,

$$
X_{N_{2}}=\frac{P_{N_{2}}}{k_{H}}=\frac{0.79 \mathrm{bar}}{9.04 \times 10^{4} \mathrm{bar}}=8.74 \times 10^{-6}
$$

The molar mass of water is $M=2(1.00794 g)+15.9994 \mathrm{~g}=18.0153 \mathrm{~g}$ In one kilogram of water, there are

$$
n_{\mathrm{H}_{2} \mathrm{O}}=\frac{1000 \mathrm{~g}}{18.0153 \mathrm{~g}}=55.5083 \mathrm{~mol}
$$

Then, from the definition of mole fraction in a binary solution

$$
n_{N_{2}}=\frac{X_{N_{2}}}{1-X_{N_{2}}} n_{H_{2} O}=\frac{8.74 \times 10^{-6}}{1-8.74 \times 10^{-6}}(55.5083 \mathrm{~mol})=4.851 \times 10^{-4} \mathrm{~mol}
$$

