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## Chemistry 2000 Spring 2019 Test 2 Version A

Time: 90 minutes

Aids permitted: calculator.

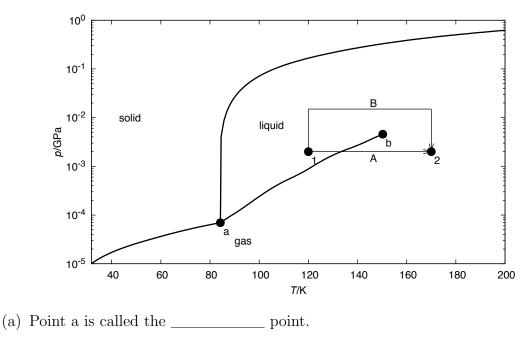
See page 10 for useful data and formulas.

- Significant figures: All answers must be given to the correct number of significant figures unless otherwise stated.
- **Units** should generally be shown in intermediate steps of a calculation. Failing to do so may result in reduced credit.
- **Overflow/scratch space:** There is extra space on pages 5 and 6, as well as a blank page just before the formula/data sheet. If you need some of this space to continue an answer, it is your responsibility to make this clear.

Question	Mark
1	/5
<b>2</b>	/8
3	/4
4	/8
5	/9
6	/8
7	/12
Total:	/54
Percentage:	%

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/5 1. Here is the phase diagram of argon:



Point b is called the \_\_\_\_\_ point. [2 marks]

(b) Consider the two paths, A and B, linking points 1 and 2 in the diagram. How does the behavior of argon along each of these two paths differ? In other words, if you were to observe a sample of argon going from point 1 to point 2 along path A, and another sample going from point 1 to point 2 along path B, what difference(s) would you notice while observing the system going through these changes? [2 marks]

(c) The triple point of argon is one of the points used to calibrate thermometers in ITS-90. Why is this a good point to use for thermometer calibration? [1 mark]

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2. When bromide ions react with permanganate ions (MnO<sub>4</sub><sup>-</sup>) in basic solution, solid manganese(IV) oxide and bromate ions (BrO<sub>3</sub><sup>-</sup>) are formed. Balance the reaction. Include states of matter for all species. [8 marks]

/4 3. In the gas phase, the following equilibrium occurs:

$$2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$$
.

(a) Calculate the standard entropy change for this reaction. [2 marks]

(b) If we start with pure NO<sub>2</sub>, some N<sub>2</sub>O<sub>4</sub> will be formed, but this will decrease the entropy since the number of gas molecules will decrease. (Your calculation should confirm this.) The second law says that the entropy should increase, so this reaction is a counterexample to the second law, i.e. it proves that the second law is wrong.

What is wrong with this argument? A qualitative counter-argument is sufficient. [2 marks]

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- 4. In this question, give your answers to a reasonable number of digits, but you do not need to track significant figures.
- (a) Calculate the equilibrium constant at 298.15 K for the reaction

$$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}.$$

[4 marks]

(b) Is the reaction thermodynamically allowed if  $p_{\rm NO} = 1.0 \times 10^{-4}$  bar,  $p_{\rm O_2} = 2.3 \times 10^{-3}$  bar, and  $p_{\rm NO_2} = 25$  bar? [4 marks]

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/9 5. At 1000 °C, the equilibrium constant for the reaction

$$FeO_{(s)} + CO_{(g)} \rightleftharpoons Fe_{(s)} + CO_{2(g)}$$

is K = 0.403. If 1.3 bar of carbon monoxide is put into a sealed flask with an excess of FeO at 1000 °C, what are the equilibrium pressures of the two gases? [9 marks]

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 $\begin{array}{ll} \mbox{/8} & 6. \ 20.5513\,{\rm g} \ {\rm of} \ {\rm carbamazepine} \ ({\rm C}_{15}{\rm H}_{12}{\rm N}_{2}{\rm O}) \ {\rm is} \ {\rm dissolved} \ {\rm in} \ 201.35\,{\rm g} \ {\rm of} \ {\rm acetone} \ ({\rm C}_{3}{\rm H}_{6}{\rm O}) \\ {\rm at} \ 20\,^{\circ}{\rm C}. \ {\rm The} \ {\rm vapor} \ {\rm pressure} \ {\rm of} \ {\rm pure} \ {\rm acetone} \ {\rm at} \ {\rm this} \ {\rm temperature} \ {\rm is} \ 0.246\,{\rm bar}. \ {\rm What} \ {\rm is} \\ {\rm the} \ {\rm vapor} \ {\rm pressure} \ {\rm of} \ {\rm the} \ {\rm solution}? \ ({\rm Carbamazepine} \ {\rm has} \ {\rm a} \ {\rm negligible} \ {\rm vapor} \ {\rm pressure}.) \\ \ [8 \ {\rm marks}] \end{array}$ 

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/12 7. The solubility, s, of a molecular substance in water is the equilibrium concentration corresponding to the process

$$A_{(s)} \rightleftharpoons A_{(aq)}.$$

The enthalpy change in this process is called (not surprisingly), the enthalpy of solution. The following table gives the solubility of caffeine at two different temperatures:<sup>1</sup>

T/K	$s/{ m mol}{ m L}^{-1}$
288.01	0.0682
328.15	0.218

In the questions that follow, try to give answers to a reasonable number of digits, but you do not need to track your significant figures.

(a) What is the enthalpy of solution of caffeine? [4 marks]

<sup>&</sup>lt;sup>1</sup>J. Zhong et al., *J. Chem. Eng. Data* **62**, 2570 (2017).

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(b) Iced coffee has become a popular drink. What is the solubility of caffeine at 0 °C? [5 marks]

- (c) Iced coffee would actually have a temperature lower than 0 °C. Why? [1 marks]
   We will ignore this effect in the rest of this question.
- (d) The concentration of caffeine in a strong cup of coffee would be about  $8 \times 10^{-3} \text{ mol } \text{L}^{-1}$ . Is it possible to precipitate out some of the caffeine when strong coffee is cooled to make iced coffee? Explain your reasoning in a few words. [2 marks]

Note: Assume that we cool the coffee by putting the cup or carafe on ice, and not by putting ice in the coffee.

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	Molar 1	masses
Constants and conversion factors	Element	$M/\mathrm{gmol^{-1}}$
$0 \text{K} = -273.15 ^{\circ}\text{C}$	Н	1.00798
$R = 8.314463 \mathrm{J}\mathrm{K}^{-1}\mathrm{mol}^{-1}$	$\mathbf{C}$	12.0106
$h = 8.514405 \mathrm{J}\mathrm{K}$ III01	Ν	14.0069
	Ο	15.9994

# Standard thermodynamic properties

Substance	$\Delta_r H^{\circ}/\mathrm{kJ}\mathrm{mol}^{-1}$	$\Delta_r G^{\circ}/\mathrm{kJ}\mathrm{mol}^{-1}$	$S^{\circ}/\mathrm{JK^{-1}mol^{-1}}$
NO <sub>(g)</sub>	90.29	86.60	210.65
$NO_{2(g)}$	33.2	51	239.9
$N_2O_{4(g)}$	9.16	97.7	304.3
O <sub>2(g)</sub>	0	0	205.0

## Formulas

$S = k_B \ln \Omega$	$\Delta S = \frac{q_{\rm rev}}{T}$
$\Delta G = \Delta H - T \Delta S$	$\Delta_r G_m = \Delta_r G_m^\circ + RT \ln Q$
$\Delta_r G_m^\circ = -RT \ln K$	$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H_m^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
$p_A = p_A^{\bullet} X_A$	$[\mathbf{A}] = k_H p_A$

### Activities

State	Activity $(a)$
Solid	1
Pure liquid	1
Ideal solvent	X
Ideal solute	$c/c^{\circ}$
Ideal gas	$p/p^{\circ}$