Final Exam: Sunday Apr 14, 2019   Name:_____

Allowed: Formula sheet (given), calculator, 3 hours

PART 1 – answer questions **1-10** in your exam booklet, **then** use your scratch card

One scratch worth **4** points; two scratches **2** points; three scratches **0.5** point (total for part 1 = 50%)

PART 2 – answer questions **11, 12 and 13** in the exam booklet provided (total for part 2 = 50%)

Qu's 1 -4: Consider n moles of an ideal gas with *adiabatic exponent* γ, initially at P_i, V_i and T_i, which reversibly undergoes an *adiabatic compression* to P_f, V_f and T_f.

1) What is the final pressure of the gas, P_f, after this process?

A. $\left(V_f / V_i\right)^{\gamma-1} P_i$ **B.** $\left(V_i / V_f\right)^{\gamma-1} P_i$ **C.** $\left(V_i / V_f\right) P_i$ **D.** $\left(V_f / V_i\right)^{\gamma} P_i$ **E.** $\left(V_i / V_f\right)^{\gamma} P_i$

2) Which of the following equations correctly relates the final temperature and volume of the gas to its initial temperature and volume?

A. $T_f^{\gamma} V_f = T_i^{\gamma} V_i$ **B.** $T_f V_f^{\gamma-1} = T_i V_i^{\gamma-1}$ **C.** $T_f^{\gamma} V_f = T_i^{\gamma} V_i$ **D.** $T_f^{\gamma} V_f = T_i^{\gamma} V_i$ **E.** $T_f V_f^{\frac{\gamma-1}{\gamma}} = T_i V_i^{\frac{\gamma-1}{\gamma}}$

3) Which of the following is the general expression for the <u>work done on the gas</u> during this process?

A. $W = \dfrac{P_i V_f}{\gamma-1}\left[\left(\dfrac{V_i}{V_f}\right)^{\gamma} - 1\right]$ **B.** $W = \dfrac{P_i V_i}{\gamma}\left[\left(\dfrac{V_i}{V_f}\right)^{\gamma-1} - 1\right]$ **C.** $W = \dfrac{P_i V_i}{\gamma}\left[\left(\dfrac{V_i}{V_f}\right)^{\gamma} - 1\right]$

D. $W = \dfrac{P_i V_i}{\gamma-1}\left[\left(\dfrac{V_f}{V_i}\right)^{\gamma-1} - 1\right]$ **E.** $W = \dfrac{P_i V_i}{\gamma-1}\left[\left(\dfrac{V_i}{V_f}\right)^{\gamma-1} - 1\right]$

4) What is the work done on one mole of helium (assumed ideal) which starts at 1 atm and $T_i = 300$ K and halves its volume?

A. 2200 J   **B.** 2900 J   **C.** 4200 J   **D.** 4900 J   **E.** 900 J

Qu's 5 -7: Some experimental data for <u>liquid mercury</u> at 1 atm and 4 °C are shown below:

Molar heat capacity at constant pressure, $c_{p,\text{Hg}}$	28.0 J/K/mol
Molar volume	1.47×10^{-5} m^3/mol
Volume thermal expansion coefficient	181×10^{-6} K^{-1}
Isothermal compressibility	3.89×10^{-11} Pa^{-1}

5) What is the molar heat capacity *at constant volume*, $c_{v,\text{Hg}}$, for liquid mercury at 4 °C ?

   A. 31.4 J/K/mol   **B.** 28.0 J/K/mol   **C.** 24.6 J/K/mol   **D.** 38.0 J/K/mol   **E.** 22.4 J/K/mol

6) What is mercury's *adiabatic compressibility* (i.e. the compressibility at constant *entropy*)?

   A. 3.4×10^{-11} Pa^{-1} **B.** 3.9×10^{-11} Pa^{-1} **C.** 2.9×10^{-11} Pa^{-1} **D.** 4.4×10^{-11} Pa^{-1} **E.** 2.4×10^{-11} Pa^{-1}

7) Meanwhile, at 1 atm and 4 °C <u>liquid water</u> has its maximum density, so a fixed amount of water at this pressure increases its volume for **both** lower and higher temperatures from this value. From this observation, what can you deduce about the molar heat capacities for liquid water ($c_{p,\text{H}_2\text{O}}$ and $c_{v,\text{H}_2\text{O}}$) at this temperature and pressure?

   A. $c_{v,\text{H}_2\text{O}} > c_{p,\text{H}_2\text{O}}$ **B.** $c_{v,\text{H}_2\text{O}} = c_{p,\text{H}_2\text{O}}$ **C.** $c_{v,\text{H}_2\text{O}} < c_{p,\text{H}_2\text{O}}$

D. $c_{p,\text{H}_2\text{O}} \rightarrow$ non-zero constant ; $c_{v,\text{H}_2\text{O}} \rightarrow 0$ **E.** $c_{p,\text{H}_2\text{O}} \rightarrow 0$; $c_{v,\text{H}_2\text{O}} \rightarrow$ non-zero constant

Qu's 8 -10: A mix of questions.

8) From consideration of the Helmholtz free energy or otherwise, which of the following quantities does $\left(\dfrac{\partial S}{\partial V}\right)_T$ equate to?

A. $\left(\dfrac{\partial P}{\partial V}\right)_T$ **B.** $\left(\dfrac{\partial T}{\partial P}\right)_V$ **C.** $\left(\dfrac{\partial P}{\partial T}\right)_V$ **D.** $\left(\dfrac{\partial V}{\partial T}\right)_P$ **E.** $\left(\dfrac{\partial V}{\partial P}\right)_T$

9) The heat capacity of liquid water at a constant pressure of 1 atm is ≈ 4200 J/kg/K . What approximate entropy change occurs when 3 kg of water is raised in temperature from $25\ °C$ to $65\ °C$ under these conditions?

A. +2.6 kJ/K **B.** −13 kJ/K **C.** +13 kJ/K **D.** −1.6 kJ/K **E.** +1.6 kJ/K

10) Which of the following are some consequences of the Third law of Thermodynamics?

A. As $T \to 0$: $\beta \to 0$, $C_v \to 0$, $C_P \to$ constant, non-zero, value

B. As $T \to 0$: $\beta \to 0$, $C_v \to$ constant, non-zero, value, $C_P \to$ constant, non-zero, value

C. As $T \to 0$: $\beta \to$ constant, non-zero, value, $C_v \to 0$, $C_P \to$ constant, non-zero, value

D. As $T \to 0$: $\beta \to 0$, $C_v \to 0$, $C_P \to 0$

E. As $T \to 0$: $\beta \to$ constant, non-zero, value, $C_v \to$ constant, non-zero, value, $C_P \to$ constant, non-zero, value

PART II – answer all three questions in exam booklet provided

11. Consider a fixed quantity of an ideal gas with a constant C_P undergoing a *Brayton cycle* (also called a *Joule cycle*), which is composed of the following four steps operating in a continuous cycle:

Step I: The gas is reversibly *adiabatically compressed* from a state P_1, V_1 to a state P_2, V_2

Step II: The gas is reversibly *isobarically expanded* to a state P_2, V_3

Step III: The gas is reversibly *adiabatically expanded* to a state P_1, V_4

Step IV: The gas is reversibly *isobarically returned* to the state P_1, V_1

a) Draw this cycle on a *PV* diagram, with arrows depicting the direction of the cycle.

b) Determine the heat flow into or out of the gas during each step, and determine, giving reasons, whether this cycle acts as a heat engine or a refrigerator.

c) Given your answer to (b) and treating γ also as a constant, find either the *coefficient of performance* of such a refrigerator, or the *efficiency* of this engine, in terms of only P_1, P_2 and γ .

12. a) State two assumptions about atoms or molecules in an *ideal gas*, and write down the equation of state of such a gas. What are the key physical differences between this gas and a *van der Waals gas*, and how are these reflected in the equation of state for the van der Waals gas?
**b)** Sketch on a *PV* diagram a typical isotherm for an ideal gas, and also the corresponding isotherm for a van der Waal gas. Identify on your diagram two differences between these isotherms.
c) For all real gases there is a particular value of *V* and *T*, called the *critical volume, V_c,* and *critical temperature, T_c,* respectively for which the T_c isotherm has a point of inflection on the *PV* diagram (i.e. zero first derivative and zero second derivative). Show that for a van der Waals gas these quantities are given by:

$$V_c = 3nb \qquad \text{and} \qquad T_c = \frac{8a}{27Rb}$$

d) The van der Waals parameters for argon are: $a = 0.1358 \text{ Pa m}^6/\text{mol}^2$ and $b = 3.2 \times 10^{-5} \text{ m}^3/\text{mol}$. For one mole of argon find V_c and T_c.
e) Given the general *PVT* surface for different phases of a single substance shown on the right, sketch a single *PV* diagram for argon that fully labels its single-phase and two-phase regions, and denote on your diagram both V_c and the particular T_c isotherm described in part (c).
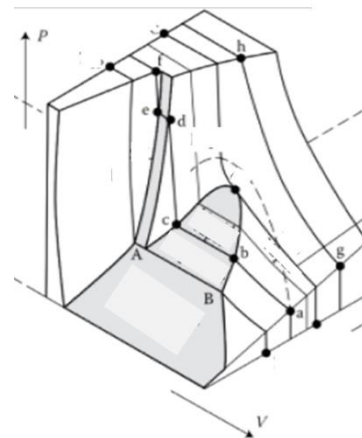
13. Consider one mole of carbon, which can exist in two common forms, either graphite or diamond. Data for each at 1 atm and 298 K are given below, where ΔH and ΔG are the change in *H* and *G* upon forming each phase from carbon in its most stable phase at this temperature and pressure:

Phase	ΔH (J)	ΔG (J)	S (J/K)	V (cm^3)
Graphite	0	0	5.74	5.31
Diamond	1895	2900	2.38	3.42

a) For a system at equilibrium at fixed pressure and temperature, which of the four thermodynamic potentials is generally minimized? Determine from this which carbon phase is most stable at 1 atm and 298 K, and also the heat released if one mole of the least stable phase changes to the most stable phase.
b) Derive the *thermodynamic identity* for enthalpy, and also for Gibbs free energy.
c) Find expressions for a system's volume, entropy, and temperature in terms of partial differentials of either *H* or *G*.
d) Assuming a linear behavior of the appropriate thermodynamic potential as the pressure changes at fixed temperature, show that the pressure at which the most stable phase of carbon changes to the other phase at 298 K occurs at $\approx 15,000 \text{ atm}$.