Name: ______________________________

Answer the questions in the spaces provided. If you run out of room for showing work, continue on the back of the page, but please write your final answer in the box.
All work should be completed on your own, and all students are expected to comply with the BU Academic Code of Conduct.
You will not need a calculator to complete this exam, and you will likely find the equation sheet at the end helpful.

Question	Points	Score
1	50	
2	50	
Total:	100	

1. (50 points) Consider the four reversible steps in the Carnot cycle of a Stirling engine expressed in fig. 1 below. All steps are reversible and involve one mole of an ideal gas. Step $1 \to 2$ the gas expands isothermally from V_1 to V_2 at high temperature T_H. Step $2 \to 3$ is isochoric (constant volume). Step $3 \to 4$ the gas is compressed isothermally from V_2 to V_1 at low temperature T_L. Step $4 \to 1$ is isochoric.

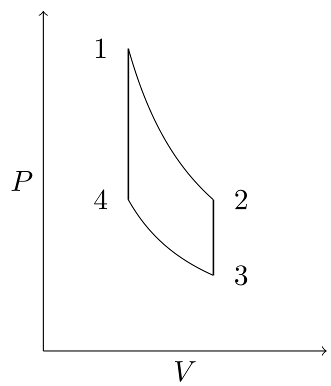

Figure 1: Carnot cycle for a Stirling engine on a pressure-volume diagram

(a) In the table below, indicate if each of the quantities q, w, ΔU, and ΔS are positive (+), negative (−), or zero (0).

	$4 \to 1$	$1 \to 2$	$2 \to 3$	$3 \to 4$
q				
w				
ΔS				
ΔU				

Solution:

	$4 \to 1$	$1 \to 2$	$2 \to 3$	$3 \to 4$
q	+	+	−	−
w	0	−	0	+
ΔS	+	+	−	−
ΔU	+	0	−	0

(b) Derive an expression for the total work done by the system in one cycle of the Stirling engine.

Solution:

$$w_{4\to1} = w_{2\to3} = 0$$

$$\begin{aligned} w_{1\to2} &= \int_1^2 P(V)\,\mathrm{d}V \\ &= \int_1^2 \frac{RT_H}{V}\,\mathrm{d}V \\ &= RT_H \ln\left(\frac{V_2}{V_1}\right) \end{aligned}$$

$$w_{3\to4} = RT_L \ln\left(\frac{V_1}{V_2}\right)$$

$$\boxed{w_{\text{total}} = R\ln\left(\frac{V_2}{V_1}\right)(T_H - T_L)}$$

(c) Suppose $V_1 = 1\,\mathrm{L}$, $V_2 = 10\,\mathrm{L}$, $T_H = 300\,\mathrm{K}$, and $T_L = 100\,\mathrm{K}$. Compute the engine's efficiency defined as the total work done by the engine divided by the heat added to the engine in step $1 \to 2$, $\eta = -w_{\text{total}}/q_{1\to2}$. (Note: the work done BY the system is the negative of the work done ON the system defined by the relation $\mathrm{d}w = -P_{\text{ext}}\,\mathrm{d}V$)

Solution:
Note, the efficiency definition given here considered w_{total} as the work done on the system even though it was defined the opposite way above, so this definition is not correct. Consequently, either sign will be accepted for the efficiency calculated.

$$q_{1\to2} = RT_H \ln\left(\frac{V_2}{V_1}\right)$$

$$\begin{aligned} \eta &= \frac{\pm R\ln\left(\frac{V_2}{V_1}\right)(T_H - T_L)}{RT_H \ln\left(\frac{V_2}{V_1}\right)} \\ &= \pm\frac{T_H - T_L}{T_H} \\ &= \pm\left(1 - \frac{1}{3}\right) \end{aligned}$$

$$\boxed{\eta = \pm\frac{2}{3}}$$

2. (50 points) Consider two ideal gas samples separated by a movable piston that can conduct heat (exchange internal energy). The total volume of the container holding the gas samples is fixed, and it is surrounded by an adiabatic boundary. The system is initially out of equilibrium. Suppose the sample in the left region of cylinder is cold, and the gas in this region is at a temperature T_c and pressure p_c. The right region contains hot gas at temperature T_h and pressure p_h.

(a) Give an expression for the entropy change, $\mathrm{d}S$, of the total system in terms of the entropy changes of the component hot and cold subsystems assuming that these entropy changes arise from exchange of heat (internal energy) between the subsystems, since the piston is thermally conductive, as well as entropy changes arising from exchange of volume between the hot and cold subsystems since the piston can move. Give your answer in terms of the cold subsystem internal energy change, $\mathrm{d}U_c$, and volume change, $\mathrm{d}V_c$.

Solution:

$$\begin{aligned}\mathrm{d}S &= \mathrm{d}S_c + \mathrm{d}S_h \\ &= \frac{1}{T_c}\,\mathrm{d}U_c + \frac{p_c}{T_c}\,\mathrm{d}V_c + \frac{1}{T_h}\,\mathrm{d}U_h + \frac{p_h}{T_h}\,\mathrm{d}V_h \\ \boxed{\mathrm{d}S} &\boxed{= \left(\frac{1}{T_c} - \frac{1}{T_h}\right)\mathrm{d}U_c + \left(\frac{p_c}{T_c} - \frac{p_h}{T_h}\right)\mathrm{d}V_c}\end{aligned}$$

(b) Suppose you want to pump heat from the cold subsystem to the hot subsystem so $\mathrm{d}U_c < 0$. What is the sign of the entropy change associated with this transfer of heat from cold to hot? Can this heat transfer occur spontaneously by itself?

Solution: Assuming constant volumes,

$$\begin{aligned}\mathrm{d}S &= (\text{big, positive} - \text{small, positive})\,\text{negative} \\ &= \text{positive} \times \text{negative} \\ &\boxed{\mathrm{d}S < 0}\end{aligned}$$

This is a $\boxed{\text{non-spontaneous}}$ process.

(c) Suppose the density of the cold ideal gas sample, $\rho_c = n_c/V_c$, on the left is higher than that of the hot gas sample on the right. If the cold gas is expanded ($\mathrm{d}V_c > 0$), so the hot gas is compressed, what is the sign of the change in entropy associated with this volume exchange? Will this volume exchange occur spontaneously?

Solution: Assuming no internal energy exchange,

$$\begin{aligned}pV &= nRT \\ p &= \rho RT \\ \mathrm{d}S &= R\,(\rho_c - \rho_h)\,\mathrm{d}V_c \\ &= (\text{big, positive} - \text{smaller, positive})\,\text{positive} \\ &= \text{positive} \times \text{positive} \\ &\boxed{\mathrm{d}S > 0}\end{aligned}$$

This is a $\boxed{\text{spontaneous}}$ process.

(d) Use your expression in (a) for the total entropy change accompanying both heat transfer and volume exchange to explain how heat can be transferred from the cold gas to the hot gas spontaneously.

Solution: Using only the two processes above—(b) is heat transfer from cold to hot and (c) is expansion of the cold with compression of the hot—the overall process of transferring heat from the cold subsystem to the hot subsystem can be accomplished spontaneously if the magnitude of positive entropy change from the volume change is larger than the magnitude of the negative entropy change from the energy transfer.

$$\boxed{\left(\frac{1}{T_c} - \frac{1}{T_h}\right) \mathrm{d}U_c > \left(\frac{p_h}{T_h} - \frac{p_c}{T_c}\right) \mathrm{d}V_c}$$

Table 1: Fundamental and derived constants

Name	Symbol	Value	Units
Atomic Mass Unit	u	$1.660\,54 \times 10^{-27}$	kg
Avogadro's Number	N_A	$6.022\,14 \times 10^{23}$	$\mathrm{mol^{-1}}$
Mass of an Electron	m_e	$9.109\,38 \times 10^{-31}$	kg
Mass of a Neutron	m_n	$1.674\,93 \times 10^{-27}$	kg
Mass of a Proton	m_p	$1.672\,62 \times 10^{-27}$	kg
Faraday's Constant	F	$9.648\,53 \times 10^{4}$	C/mol
Gas Constant	R	8.314 46	J/(K mol)
		0.082 06	L atm/(K mol)
		62.363 58	L Torr/(K mol)
Boltzmann's Constant	k_B	$1.380\,65 \times 10^{-23}$	J/K
Planck's Constant	h	$6.626\,07 \times 10^{-34}$	J s
Speed of Light	c	$2.997\,92 \times 10^{8}$	m/s
Earth's Gravitational Constant	g	9.806 65	$\mathrm{m/s^2}$
Bohr Radius	a_0	$5.291\,77 \times 10^{-11}$	m
Rydberg Constant	R_∞	$1.097\,37 \times 10^{7}$	$\mathrm{m^{-1}}$
Hartree Energy	E_h	$4.359\,74 \times 10^{-18}$	J

Table 2: Formulas

$$\ln 2 = 0.693$$

$$\ln 3 = 1.099$$

$$\ln 5 = 1.609$$

$$\ln N! \approx N \ln N - N$$

$$\Delta U = q + w$$

$$H = U + PV$$

$$q = mc_s \Delta T$$

$$q_{\text{calorimeter}} = C_{\text{calorimeter}} \Delta T$$

$$c_P = c_V + R$$

$$c_P = \frac{5}{2} R$$

$$c_V = \frac{3}{2} R$$

$$\Delta U = nc_V \Delta T$$

$$\Delta H = nc_P \Delta T$$

$$w = -\int_{V_1}^{V_2} P_{\text{ext}}(V)\,\mathrm{d}V$$

$$w = -nRT \ln\left(\frac{V_2}{V_1}\right)$$

$$w = -P_{\text{ext}} \Delta V$$

$$\Delta S_{\text{sys}} = \int_1^2 \frac{\mathrm{d}q_{\text{rev}}}{T}$$

$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T}$$

$$\Delta S_{\text{sys}} = nR \ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T_{\text{surr}}}$$

$$\Delta S_{\text{sys}} = nc_P \ln\left(\frac{T_2}{T_1}\right)$$

$$\Delta S_{\text{sys}} = nc_V \ln\left(\frac{T_2}{T_1}\right)$$

$$\int_0^\infty \mathrm{e}^{-\alpha x}\,\mathrm{d}x = \frac{1}{\alpha}$$

$$\int_0^\infty \mathrm{e}^{-\alpha x^2}\,\mathrm{d}x = \frac{1}{2}\sqrt{\frac{\pi}{\alpha}}$$

$$\int_0^\infty x\mathrm{e}^{-\alpha x^2}\,\mathrm{d}x = \frac{1}{2\alpha}$$

$$\int_0^\infty x^2\mathrm{e}^{-\alpha x^2}\,\mathrm{d}x = \frac{1}{4}\sqrt{\frac{\pi}{\alpha^3}}$$

$$N! \approx \left(\frac{N}{\mathrm{e}}\right)^N$$

$$f(x) = \sum_{i=0}^{\infty} \frac{1}{i!} \left.\frac{\mathrm{d}^i f(x)}{\mathrm{d}x^i}\right|_{x=a} (x-a)^i$$