Guidance: Please answer each question to the best of your ability. Make sure your response is **legible**, **precise**, includes relevant dimensional **units** (where appropriate), logically presented (include non-mathematical language in addition to mathematical language if necessary to convey your intent clearly and transparently), and **state all assumptions** you invoke. You are free to use your Equations Handbook, calculator, and writing instrument of your choice. If you have any doubt(s) about the meaning/intent of a question(s), please ask immediately so you do not wander off on an incorrect path. Please **do not** ask your colleague to borrow their Handbook or calculator or writing instrument.

1	/20
2	/20
3	/20
4	/20
5	/20
Extra Credit	/5
Total	/100

1 (20 Points). Since enthalpy is a state function, it can be written as a function of the state variables temperature (T) and pressure (P), H(P,T). Thus, the total differential of enthalpy of a substance (solid, liquid, gas) can be expressed as:

$$dH(P,T) = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

The constant pressure heat capacity of a substance is defined as $C_P(T) = \left(\frac{\partial H}{\partial T}\right)_P$. Consider a 143.0 gram sample of graphite heated from 300K to 600K at constant pressure conditions. The variation of graphite's molar heat capacity with temperature over this temperature range is given by:

$$C_{P,molar}(T) = -12.19 + 0.1126T - 0.0001947T^2 + 1.919 \times 10^{-7}T^3 - 7.800 \times 10^{-11}T^4$$

1A. Compute numerical values for ΔH and q_P for this process.

Given: graphite (solid carbon); constant pressure heating; $C_{p,m}(T)$ given

ΔH: $dH(P,T) = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = \left(\frac{\partial H}{\partial T}\right)_P dT$ (since $dP = 0$)

$$\Delta H = \int_{T_1}^{T_2} dH(P,T) = \int_{T_1}^{T_2} \left(\frac{\partial H}{\partial T}\right)_P dT = \int_{T_1}^{T_2} n\, C_{p,m}(T)\, dT$$

$$\Delta H = n \int_{T_1}^{T_2} \left[-12.19 + 0.1126\,T - 0.0001947\,T^2 + 1.919 \times 10^{-7}\,T^3 - 7.8 \times 10^{-11}\,T^4 \right] dT$$

$$\Delta H = n \left[-12.19\,T + \left(\tfrac{1}{2}\right)(0.1126)\,T^2 - \left(\tfrac{1}{3}\right)(0.0001947)\,T^3 + \left(\tfrac{1}{4}\right)(1.919 \times 10^{-7})\,T^4 - \left(\tfrac{1}{5}\right)(7.8 \times 10^{-11})\,T^5 \right]_{T_1}^{T_2}$$

$$T_1 = 300\,K \quad ; \quad T_2 = 600\,K \quad ; \quad n = \frac{143.0\,gr}{12\,gr/mole}$$

$$\boxed{\Delta H = 46.9\ kJ}$$

We know that: $dU = dq - P_{ext}\,dV \implies dq = dU + P_{ext}\,dV$
$$dq = d(U + P_{ext}V)$$

assuming reversible heating:
$$dq_P = d(U + PV) = dH \qquad \therefore \boxed{q_P = \Delta H}$$

2 (20 Points). Consider a Carnot Engine (with ideal gas as fluid) operating cyclically and reversibly between 4 equilibrium states. The cycle consists of an isothermal expansion from state 1 to state 2 at temperature T_{Hot}; an adiabatic expansion from state 2 to state 3; an isothermal compression from state 3 to state 4 at temperature T_{Cold}; and a final adiabatic compression from state 4 to state 1.

2A. For each leg of the cycle, compute $\int_{?}^{?} \dfrac{dq_{reversible}}{T}$. You will have to determine the limits of integration based on the information given and your knowledge of thermodynamics and the Carnot Cycle (Carnot Engine).

P

V
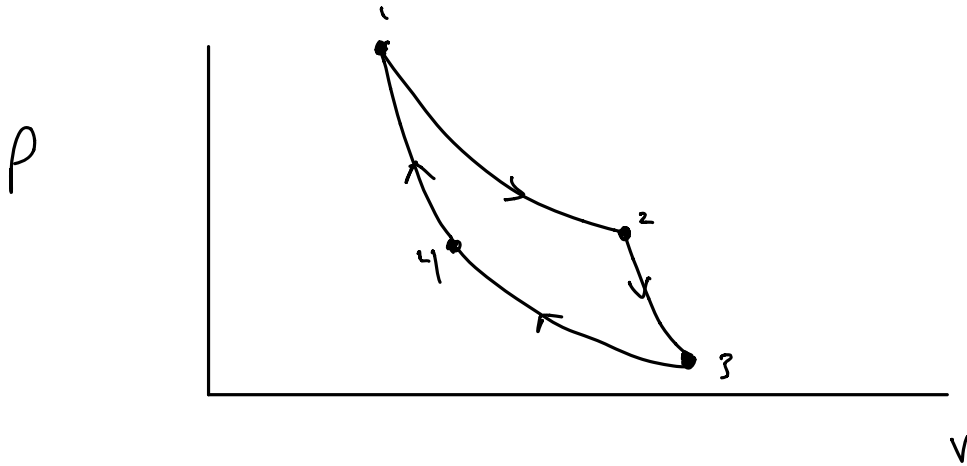
$\underline{1 \to 2}$: Isothermal $\to dU = 0$

$$dq_{rev} = -dW_{rev} = p\,dV = nRT\,d(\ln V)$$

$$\frac{dq_{rev}}{T} = nR\,d(\ln V)$$

$$\int \frac{dq_{rev}}{T} = nR \int_{V_1}^{V_2} d(\ln V) = \underline{\underline{nR \ln\left(\frac{V_2}{V_1}\right)}}$$

$2 \to 3$: Adiabatic $\to dq_{rev} = 0$ $\quad \therefore \underline{\underline{\int \frac{dq_{rev}}{T} = 0}}$

$4 \to 1$: Adiabatic $\to dq_{rev} = 0$ $\quad \therefore \underline{\underline{\int \frac{dq_{rev}}{T} = 0}}$

$3 \to 4$: Isothermal $\to dU = 0$

$$dq_{rev} = -dW_{rev} = p\,dV = nRT\,d(\ln V)$$

$$\frac{dq_{rev}}{T} = nR\,d(\ln V)$$

$$\int \frac{dq_{rev}}{T} = nR \int_{V_3}^{V_4} d(\ln V) = \underline{\underline{nR \ln\left(\frac{V_4}{V_3}\right)}}$$

2B. Based on your work of Part 2A, discuss your result.

From 2A, we have :

$$\oint \frac{dq_{rev}}{T} = nR \ln\left(V_2/V_1\right) + nR \ln\left(V_4/V_3\right)$$

Recall! for adiabatic, reversible process $\left(2 \to 3 \ \& \ 4 \to 1\right)$

$$P_2 V_2^{\gamma} = P_3 V_3^{\gamma} \qquad P_4 V_4^{\gamma} = P_1 V_1^{\gamma} \qquad \left(\gamma = c_p/c_v\right)$$

$$\frac{P_2 V_2^{\gamma}}{P_1 V_1^{\gamma}} = \frac{P_3 V_3^{\gamma}}{P_4 V_4^{\gamma}} \implies \left(\frac{V_2}{V_1}\right)^{\gamma} = \left(\frac{P_1 P_3}{P_2 P_4}\right)\left(\frac{V_3}{V_4}\right)^{\gamma}$$

$$= \left(\frac{nRT_H}{V_1} \frac{nRT_c}{V_3} \frac{V_2}{nRT_H} \frac{V_4}{nRT_c}\right)\left(\frac{V_3}{V_4}\right)^{\gamma}$$

$$\left(\frac{V_2}{V_1}\right)^{\gamma} = \left(\frac{V_2 V_4}{V_1 V_3}\right)\left(\frac{V_3}{V_4}\right)^{\gamma}$$

$$\therefore \left(\frac{V_2}{V_1}\right)^{\gamma-1} = \left(\frac{V_3}{V_4}\right)^{\gamma-1}$$

$$\therefore \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

So! $\oint \frac{dq_{rev}}{T} = nR \ln\left(V_2/V_1\right) + nR \ln\left(V_4/V_3\right)$

$$= nR \ln\left(V_2/V_1\right) - nR \ln\left(V_3/V_4\right)$$

$$= nR \ln\left(V_2/V_1\right) - nR \ln\left(V_2/V_1\right)$$

$$= \underline{\underline{0}}$$

seems like $\frac{dq_{rev}}{T}$ is a State function

3 (20 Points). An automobile tire contains air at 225000 Pa pressure and temperature of 25 C. The stem valve is removed and air flows out adiabatically against a constant external pressure of 1 bar. The final pressure of the air is 1 bar. What is the final temperature? For air, the molar constant volume heat capacity is 2.5R where R is the ideal gas constant. Please state any assumption(s) you invoke.

Given: ideal gas; $P_i = 225 \times 10^3$ Pa; $T_i = 25\,°C = 298.15\,K$

$$P_{ext} = 1\ bar \qquad P_f = 1\ bar \quad ; \quad adiabatic$$

1st "Law":

$$dU = dq + dW = dW$$

$$C_v\, dT = -P_{ext}\, dV$$

$$n\, C_{v,molar}\, dT = -P_{ext}\, dV$$

$$P_{ext} = constant$$

$$\therefore \quad n\, C_{v,molar}\, (T_f - T_i) = -P_{ext}\,(V_f - V_i)$$

$$n\, C_{v,molar}\,(T_f - T_i) = -P_{ext}\left(\frac{nRT_f}{P_f} - \frac{nRT_i}{P_i}\right)$$

$$2.5\,(T_f - T_i) = \left(\frac{-P_{ext}}{P_f}\right)(T_f) + \left(\frac{P_{ext}}{P_i}\right) T_i$$

$$2.5\,T_f - 2.5\,T_i = \left(-\frac{1\,bar}{1\,bar}\right) T_f + \left(\frac{1\,bar}{225\times10^3\,Pa}\right)\!\left(----\right) T_i$$

$$3.5\,T_f = 2.5\,T_i + \left(\frac{1\,bar}{225\times10^3\,Pa}\right)\!\left(\frac{Pa}{bar}\right) T_i$$

$$T_f = \frac{1}{3.5}\left[2.5\,T_i + \left(\frac{1\,bar}{225\times10^3\,Pa}\right)\!\left(\frac{10^5\ Pa}{1\ bar}\right) T_i\right]$$

$$= \frac{1}{3.5}\left[T_i\left(2.5 + \frac{10^5}{225}\right)\right]$$

$$\boxed{T_f = 0.841\,T_i = 250.8\,K}$$

4 (20 Points) In class, we showed that the ideal Carnot efficiency is $\eta_{Carnot} = 1 + \dfrac{q_C}{q_H}$. Show how we can arrive at an expression that is a function of temperatures T_C and T_H only (the final form will include constant numerical values).

$$\eta_{Carnot} = 1 + \frac{q_c}{q_H}$$

$$q_c = nRT_c \ln\left(V_4/V_3\right)$$

$$q_H \approx nRT_H \ln\left(V_2/V_1\right)$$

Recalling exam problem 2B :

$$P_2 V_2^\gamma = P_3 V_3^\gamma$$

$$P_1 V_1^\gamma = P_4 V_4^\gamma$$

Taking ratio of these 2 equations :

$$\left(\frac{V_2}{V_1}\right)^\gamma = \left(\frac{P_1 P_3}{P_2 P_4}\right) \left(\frac{V_3}{V_4}\right)^\gamma$$

$$= \left(\frac{nRT_H \; nRT_c \; V_2 V_4}{nRT_H \; nRT_c \; V_1 V_3}\right) \left(\frac{V_3}{V_4}\right)^\gamma$$

$$= \left(\frac{V_2 V_4}{V_1 V_3}\right) \left(\frac{V_3}{V_4}\right)^\gamma$$

$$\therefore \left(\frac{V_2}{V_1}\right)^{\gamma-1} = \left(\frac{V_3}{V_4}\right)^{\gamma-1} \implies \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

So! $\eta_{Carnot} = 1 + \dfrac{q_c}{q_H} = 1 + \left(\dfrac{nRT_c}{nRT_H}\right) \left[\dfrac{\ln\left(V_4/V_3\right)}{\ln\left(V_2/V_1\right)}\right]$

$$\underbrace{\phantom{\dfrac{\ln\left(V_4/V_3\right)}{\ln\left(V_2/V_1\right)}}}_{= -1}$$

$$\boxed{\eta_{Carnot} = 1 - \frac{T_c}{T_H}}$$

4B. If an automobile engine burns gasoline at a temperature of 1089K and the ambient temperature is 294K, what is the theoretical maximum Carnot efficiency of this particular engine?

$$\eta_{Carnot} = 1 - \frac{T_c}{T_H} = 1 - \frac{294\ K}{1089\ K}$$

$$\eta_{Carnot} = 0.73$$

$$or\quad 73\ \%$$

5 (20 Points) Short answers

A. For differential heat interactions, $dq_{irreversible} < dq_{reversible}$: True or False _____ **True** _____

B. For differential work interactions, $dw_{irreversible} < dw_{reversible}$: True or False _____ **False** _____

C. In a system composed of 3 ideal gases with mole fractions y_1, y_2, y_3, and maintained at total constant pressure P (and temperature T), what is the partial pressure of each species?

$$P_1 = y_1 P \quad ; \quad P_2 = y_2 P \quad ; \quad P_3 = y_3 P$$

D. Give the equality: $\ln\left(\dfrac{P_1}{P_2}\right) =$ $\ln(P_1) - \ln(P_2) = -[\ln(P_2) - \ln(P_1)]$

$\nwarrow$ or $\nearrow$

E. For a function, G(n,P,T), provide an expression for the **total differential** of G(n,P,T) in terms of appropriate partial derivatives. Make sure to specify what is held constant in each partial derivative using proper notation.

$$dG(n,P,T) = \left(\frac{\partial G}{\partial n}\right)_{P,T} dn + \left(\frac{\partial G}{\partial T}\right)_{P,n} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n} dP$$

Extra Credit (5 Points)

If

$$d\mu(P,T) = \left(\frac{\partial \mu}{\partial T}\right)_P dT + (nRT)\, d(\ln P)$$

what is $\mu(P_2,T) - \mu(P_1,T) = ?$

$$d\mu(P,T) = \left(\frac{\partial \mu}{\partial T}\right)_P dT + nRT\, d\left(\ln P\right)$$

$$\mu(P_2,T) - \mu(P_1,T) = \Delta\mu \quad @ \text{ constant temperature}$$

$$d\mu = nRT\, d\left(\ln P\right)$$

$$\int d\mu = \mu_2(P_2,T) - \mu(P_1,T) = nRT \ln\left(\frac{P_2}{P_1}\right)$$

$$\Delta\mu = nRT\left(\ln P_2 - \ln P_1\right)$$