ChemE 2200 - Physical Chemistry II for Engineers
Solution to Second Preliminary Examination - 2025

1.(A) Calculate the total work during a cycle. $w = 0$ for path DA because $\Delta V = 0$. For the adiabatic paths AB and CD, $q = 0$, so

$$w = \Delta U = \int C_V dT = C_V(\Delta T)$$

because the heat capacity is independent of temperature for an ideal gas at modest temperatures. The work for the isobaric expansion is $w_{BC} = -P_B(V_C - V_B)$. Thus the total work for the cycle is

$$\begin{aligned} w &= w_{AB} + w_{BC} + w_{CD} + w_{DA} \\ &= C_V(T_B - T_A) - P_B(V_C - V_B) + C_V(T_D - T_C) + 0 \\ &= C_V(T_B + T_D - T_A - T_C) - P_B(V_C - V_B) \end{aligned}$$

Because the gas is ideal and $P_B = P_C$, $P_B V_B = nRT_B$ and $P_C V_C = P_B V_C = nRT_C$,

$$\begin{aligned} w &= C_V(T_B + T_D - T_A - T_C) - nR(T_C - T_B) \\ &= (C_V + nR)(T_B - T_C) + C_V(T_D - T_A) \\ &= C_P(T_B - T_C) + C_V(T_D - T_A) \end{aligned}$$

Calculate the heat delivered along path BC.

$$\begin{aligned} q_{BC} &= \Delta U_{BC} - w_{BC} = C_V(T_C - T_B) - (-P_B(V_C - V_B)) \\ &= C_V(T_C - T_B) + P_B(V_C - V_B) \\ &= C_V(T_C - T_B) + nR(T_C - T_B) \\ &= (C_V + nR)(T_C - T_B) \\ &= C_P(T_C - T_B) \end{aligned}$$

To calculate the efficiency, note that the work done by the system is $-w_{\text{cycle}}$ because of the convention for w; w is positive for work done by the surroundings on the system. The efficiency is therefore

$$\begin{aligned} \varepsilon &= \frac{-w_{\text{cycle}}}{q_{BC}} = \frac{-\left[C_P(T_B - T_C) + C_V(T_D - T_A)\right]}{C_P(T_C - T_B)} \\ &= \frac{-C_P(T_B - T_C)}{C_P(T_C - T_B)} + \frac{-C_V(T_D - T_A)}{C_P(T_C - T_B)} \\ &= 1 - \frac{C_V(T_D - T_A)}{C_P(T_C - T_B)} \end{aligned}$$

Some calculated a numerical value for $P_B(V_C - V_B)$ rather than convert to temperatures. The numerical value is

$$\begin{aligned} P_B(V_C - V_B) &= nP_B(\overline{V}_C - \overline{V}_B) = n(14\text{ atm})(8.8 - 4.3\text{ L/mol}) = n63\text{ L}\cdot\text{atm/mol} \\ &= n63\text{ L}\cdot\text{atm/mol} \times 101.3\text{ J/L}\cdot\text{atm} \\ &= n6.4\text{ kJ/mol} \end{aligned}$$

Only two significant figures can be justified. Some answers claimed five figures were significant.

This cycle is a Diesel heat engine. A mixture of fuel + air is compressed adiabatically along path AB. The mixture ignites spontaneously and combusts as the gas expands at constant pressure along path BC. The heat delivered to the cycle is chemical energy from the combustion. The hot combustion gas expands adiabatically along path CD. The combustion gas is expelled at constant volume along path DA. Finally, A mixture of fuel and air is injected into the cylinder at point A and the cycle repeats.

(B) Paths AB and CD are adiabatic and reversible, so $\Delta S = 0$; the paths are vertical on a *T*-*S* map. Path DA connects points A and D but the line is curved. From a Useful Relationship we have

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_\mathrm{V}}{T}$$

Or in terms of the slope on the *S*-*T* plot,

$$\left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_\mathrm{V}}$$

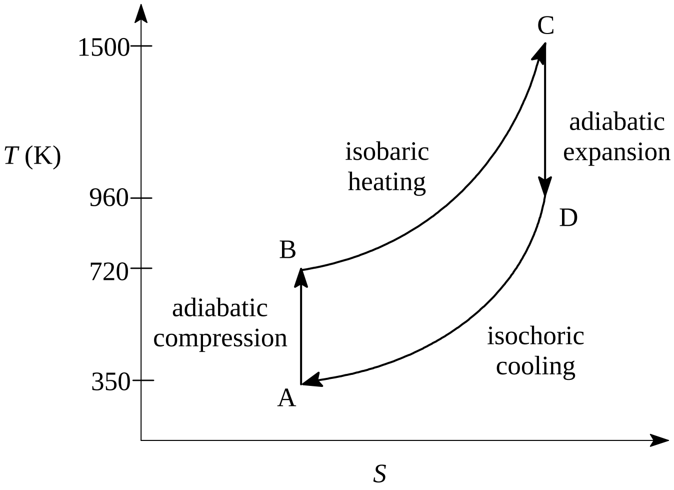
Because C_V is constant for an ideal gas, the slope increases with temperature and the path is curved. Path BC connects points B and C, but again the line is curved. From a Useful Relationship we have

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_\mathrm{P}}{T}$$

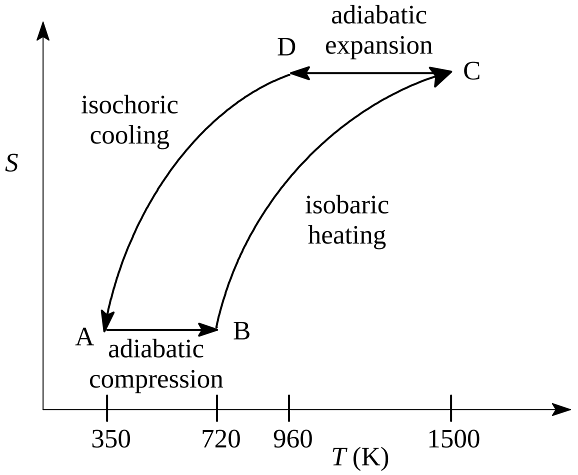
Or in terms of the slope on the *S*-*T* plot,

$$\left(\frac{\partial T}{\partial S}\right)_P = \frac{T}{C_\mathrm{P}}$$

The temperature is higher, which increases the slope, but C_P is greater than C_V which decreases the slope. However, C_P is at most a factor of 5/3 greater, whereas the temperature is about 2 times greater.



Some switched the axes from the conventional representation shown above. In this case, the trajectories on a *S*-*T* map are -



Grading Rubric:

(A) Expresssion for heat engine efficiency: $\varepsilon = \dfrac{-w_{\text{cycle}}}{q_{\text{in}}}$	3 points
Expresssions for w_{AB}, w_{BC}, w_{CD}, and w_{DA} in terms of T:	3 points each
Expression for q_{BC} in terms of T:	5 points
Points deducted:	
used w_{cycle} instead of $-w_{\text{cycle}}$:	–2 points
included q_{DA} in q_{in}:	–4 points
missing '*n*' in numerical value for $P_{\text{B}}(V_{\text{C}}-V_{\text{B}})$:	–1 point
inaccurate numerical value for $P_{\text{B}}(V_{\text{C}}-V_{\text{B}})$:	–1 point
incorrect units for numerical value for $P_{\text{B}}(V_{\text{C}}-V_{\text{B}})$:	–1 point

(B) Trajectory AB goes up vertically:	3 points
Trajectory BC increases to the right	3 points
Trajectory CD goes down vertically:	3 points
Trajectory DA decreases to the left	3 points
Used $\left(\dfrac{\partial S}{\partial T}\right)_V = \dfrac{C_{\text{V}}}{T}$ and $\left(\dfrac{\partial S}{\partial T}\right)_P = \dfrac{C_{\text{P}}}{T}$ to predict slopes of BC and DA:	3 points

2.(A) We need to calculate the change in S caused by a change in temperature, with volume constant. Assume the heating is reversible. Start with the practical equation for S in terms of temperature and volume.

$$dS = \frac{C_{\text{V}}}{T}dT + \left(\frac{\partial P}{\partial T}\right)_V dV$$

At constant volume, the second term drops. Integrate the dT term.

$$dS = \frac{C_{\text{V}}}{T}dT$$

$$\Delta S = \int_{T_1}^{T_2}\frac{n\overline{C}_{\text{V}}}{T}dT = n\overline{C}_{\text{V}}\ln\frac{T_2}{T_1}$$

Substitute $\overline{C}_{\text{V}} = 3/2R$ for an ideal monatomic gas and substitute the temperatures.

$$\Delta S = (1\,\text{mol})\left(\frac{3}{2}\right)(8.314\ \text{J/K}\cdot\text{mol})\ln\frac{500\ \text{K}}{300\ \text{K}} = 6.37\ \text{J/K}$$

If you used a different equation derived for isochoric heating,

$$\Delta S = nR\ln\frac{V_2}{V_1}$$

as noted in thermodynamics lecture 4, slide 16, for an isochoric process at V_2, V_1 is the volume at the intersection of an isothermal path at T_2 (= 500 K) and an adiabatic path through V_2 and T_1.

(B) We need to calculate the change in S caused by a change in temperature, with pressure constant. Again assume the heating is reversible. Start with the practical equation for S in terms of pressure and volume.

$$dS = \frac{C_{\text{P}}}{T}dT - \left(\frac{\partial V}{\partial T}\right)_P dP$$

At constant pressure, the second term drops. Integrate the dT term.

$$dS = \frac{C_\mathrm{P}}{T}\,dT$$

$$\Delta S = \int_{T_1}^{T_2} \frac{n\overline{C}_\mathrm{P}}{T}\,dT = n\overline{C}_\mathrm{P} \ln\frac{T_2}{T_1}$$

Substitute $\overline{C}_\mathrm{P} = 5/2R$ for an ideal monatomic gas and substitute the temperatures.

$$\Delta S = (1\ \mathrm{mol})\left(\frac{5}{2}\right)(8.314\ \mathrm{J/K\cdot mol})\ln\frac{500\ \mathrm{K}}{300\ \mathrm{K}} = 10.62\ \mathrm{J/K}$$

Again if you used a different equation derived for isobaric heating,

$$\Delta S = \int_{T_1}^{T_2} \frac{n\overline{C}_\mathrm{V}}{T}\,dT + nR\ln\frac{V_2}{V_1}$$

again, for an isochoric process at V_2, V_1 is the volume at the intersection of an isothermal path at T_2 (= 500 K) and an adiabatic path through V_2 and T_1.

(C) This question is similar to exercise 1(C) of Homework 6. When the system is heated at constant volume, the system does no work; heat is supplied to only to heat the gas. When the system is heated at constant pressure, the system does work; heat is supplied to heat the gas *and* do work as the system expands. Because $\Delta S = q_\mathrm{rev}/T$, more heat supplied causes a larger entropy increase.

Stated differently, the internal energy of an ideal gas depends on temperature only. Because both gases are heated to 500 K from 300 K, $\Delta U_\mathrm{isochoric} = \Delta U_\mathrm{isobaric}$ $\Delta U = q + w$ and no work is done for the isochoric ($\Delta V = 0$) heating, so $q_\mathrm{isochoric} < q_\mathrm{isobaric}$. Because $\Delta S = q_\mathrm{rev}/T$, more heat delivered during the isobaric heating causes a larger ΔS.

It is insufficient to explain the difference is because $C_\mathrm{P} > C_\mathrm{V}$ in the equations used to calculate ΔS.

It is insufficient to explain the difference is because $dS = \frac{C_\mathrm{V}}{T}dT + \left(\frac{\partial P}{\partial T}\right)_V dV$ and the second term is zero for isochoric heating, but the second term is a positive quantity for isobaric heating, so $\Delta S_\mathrm{isochoric} < \Delta S_\mathrm{isobaric}$.

Grading Rubric:

(A) 8 points

(B) 8 points

Points deducted:

Missing units for (A) or (B)	−1 point
Incomplete units; J instead of J/K	–½ point

(C) 9 points

3. One approach is to start with the definition of C_P,

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

$$\left(\frac{\partial C_\mathrm{P}}{\partial P}\right)_T = \left[\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial T}\right)_P\right]_T = \left[\frac{\partial}{\partial T}\left(\frac{\partial H}{\partial P}\right)_T\right]_P \qquad (1)$$

Use the Practical Equation for dH to obtain an expression for $(\partial H/\partial P)_T$.

$$dH = C_\mathrm{P}dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]dP$$

Apply constant T, which eliminates the first term on the right.

$$dH = \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]dP \qquad \text{at constant } T$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P \qquad (2)$$

Substitute equation (2) into equation (1) and expand the differentiation on the right.

$$\left(\frac{\partial C_\mathrm{P}}{\partial P}\right)_T = \left[\frac{\partial}{\partial T}\left(V - T\left(\frac{\partial V}{\partial T}\right)_P\right)\right]_P \qquad (3)$$

$$= \left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial T}{\partial T}\right)_P\left(\frac{\partial V}{\partial T}\right)_P - T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

Note that $(\partial T/\partial T)_p = 1$, so the first two terms on the right cancel.

$$\left(\frac{\partial C_\mathrm{P}}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial V}{\partial T}\right)_P - T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

$$\left(\frac{\partial C_\mathrm{P}}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

Another approach is to start with the Practical Equation for *dH*,

$$dH = C_\mathrm{P}dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]dP$$

and apply Euler's theorem for an exact differential

$$\left(\frac{\partial C_\mathrm{P}}{\partial P}\right)_T = \left[\frac{\partial}{\partial T}\left(V - T\left(\frac{\partial V}{\partial T}\right)_P\right)\right]_P$$

This equation is the same as equation (3) above. The derivation from here is the same as above.

Yet another approach begins with a Useful Relation

$$\frac{C_\mathrm{P}}{T} = \left(\frac{\partial S}{\partial T}\right)_P$$

$$C_\mathrm{P} = T\left(\frac{\partial S}{\partial T}\right)_P$$

Take the partial derivative with respect to *T* at constant *P*.

$$\left(\frac{\partial C_\mathrm{P}}{\partial P}\right)_T = \left[\frac{\partial}{\partial P}T\left(\frac{\partial S}{\partial T}\right)_P\right]_T$$

$$\left(\frac{\partial C_\mathrm{P}}{\partial P}\right)_T = \left(\frac{\partial T}{\partial P}\right)_T\left(\frac{\partial S}{\partial T}\right)_P + T\left[\frac{\partial}{\partial P}\left(\frac{\partial S}{\partial T}\right)_P\right]_T$$

The first term on the right is zero. Apply the commutative property of partial differentiation to the second term.

$$\left(\frac{\partial C_\mathrm{P}}{\partial P}\right)_T = T\left[\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial P}\right)_T\right]_P$$

Substitute the following Maxwell relation into the term on the right.

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial C_\mathrm{P}}{\partial P}\right)_T = T\left[\frac{\partial}{\partial T}\left[-\left(\frac{\partial V}{\partial T}\right)_P\right]\right]_P$$

$$\left(\frac{\partial C_\mathrm{P}}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

Grading Rubric:

Used 1st hint: Wrote the equation suggested by the hint:	2 points
Derived equation (1)	5 points
Derived equation (2)	5 points
Derived equation (3)	5 points
Derived relation to be proven:	3 points

Analogous points for a derivation that started with the second hint.

4. Use the Clausius-Clapeyron equation. Thus we assume $\Delta\overline{V}_\text{transition} = \overline{V}_\text{steam} - \overline{V}_\text{water} \approx \overline{V}_\text{steam}$ for the water-steam transition at 1 atm. This assumption is verified by the data given; the error is < 0.06%.

$$\frac{d(\ln P)}{dT} = \frac{\Delta\overline{H}_\text{vap}}{RT^2}$$

Separate and integrate, and assume $\Delta\overline{H}_\text{vap}$ is constant in the range 100 to 120ºC.

$$\int d(\ln P) = \int \frac{\Delta\overline{H}_\text{vap}}{RT^2}\,dT$$

$$\ln\frac{P_2}{P_1} = -\frac{\Delta\overline{H}_\text{vap}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

$$P_2 = P_1 \exp\left[-\frac{\Delta\overline{H}_\text{vap}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\right]$$

Substitute $T_1 = 373$ K, $T_2 = 393$ K, and $P_1 = 1$ atm.

$$P_2 = (1\,\text{atm})\exp\left[-\frac{40.6\ \text{kJ/mol}}{0.008314\ \text{kJ/K}\cdot\text{mol}}\left(\frac{1}{393\ \text{K}}-\frac{1}{373\ \text{K}}\right)\right]$$

$$P_2 = (1\,\text{atm})e^{+0.666} = 1.95\ \text{atm}$$

It is less accurate to calculate the slope of the liquid-vapor border on a *P*-*V* phase map at 100ºC and multiply by the temperature increase ($\Delta T = 20$ºC) to find the pressure increase. One less-accurate method calculated the slope $d(\ln P)/dT$ at 100ºC.

$$\frac{d(\ln P)}{dT} \approx \frac{\Delta(\ln P)}{\Delta T} \approx \frac{\Delta\overline{H}_\text{vap}}{RT^2} = \frac{40.6\ \text{kJ/mol}}{(0.008314\ \text{kJ/K}\cdot\text{mol})(373\ \text{K})^2} = 0.0351/\text{K}$$

$$\Delta(\ln P) = (0.0351/\text{K})\Delta T = (0.0351/\text{K})(20\ \text{K}) = 0.070$$

$$\ln\frac{P}{1\ \text{atm}} = 0.070$$

$$P = e^{0.070}(1\ \text{atm}) = 2.02\ \text{atm}$$

The error is only 4%. A better estimate is obtained by using the average temperature, 383 K instead of 373 K.

$$\frac{d(\ln P)}{dT} \approx \frac{\Delta(\ln P)}{\Delta T} \approx \frac{\Delta \overline{H}_{\text{vap}}}{RT^2} = \frac{40.6\ \text{kJ/mol}}{(0.008314\ \text{kJ/K}\cdot\text{mol})(383\ \text{K})^2} = 0.0333/\text{K}$$

$$\Delta(\ln P) = (0.0333/\text{K})\Delta T = (0.0333/\text{K})(20\ \text{K}) = 0.666$$

$$\ln\frac{P}{1\ \text{atm}} = 0.666$$

$$P = e^{0.666}(1\ \text{atm}) = 1.95\ \text{atm}$$

A more severe error results from calculating the slope *dP*/*dT* at 100ºC.

$$\frac{d(\ln P)}{dT} = \frac{1}{P}\frac{dP}{dT} = \frac{\Delta \overline{H}_{\text{vap}}}{RT^2}$$

$$\frac{\Delta P}{\Delta T} = P\frac{\Delta \overline{H}_{\text{vap}}}{RT^2} = (1\ \text{atm})\frac{40.6\ \text{kJ/mol}}{(0.008314\ \text{kJ/K}\cdot\text{mol})(373\ \text{K})^2} = 0.0351\ \text{atm/K}$$

$$\Delta P = (0.0351\ \text{atm/K})\Delta T = (0.0351\ \text{atm/K})(20\ \text{K}) = 0.702\ \text{atm}$$

$$P - 1\ \text{atm} = 0.702\ \text{atm}$$

$$P = 1.70\ \text{atm}$$

This approach yields an error of −13%. The estimate is slightly worse when the average temperature, 383 K, is used instead of 373 K.

$$\frac{d(\ln P)}{dT} = \frac{1}{P}\frac{dP}{dT} = \frac{\Delta \overline{H}_{\text{vap}}}{RT^2}$$

$$\frac{\Delta P}{\Delta T} = P\frac{\Delta \overline{H}_{\text{vap}}}{RT^2} = (1\ \text{atm})\frac{40.6\ \text{kJ/mol}}{(0.008314\ \text{kJ/K}\cdot\text{mol})(383\ \text{K})^2} = 0.0333\ \text{atm/K}$$

$$\Delta P = (0.0333\ \text{atm/K})\Delta T = (0.0333\ \text{atm/K})(20\ \text{K}) = 0.666\ \text{atm}$$

$$P - 1\ \text{atm} = 0.666\ \text{atm}$$

$$P = 1.67\ \text{atm}$$

Grading Rubric:

Omitted key assumptions	−1 point
Assumed ΔV_{vap} was constant, which yields $P = 1.70$ atm	−1 point
Using the slope *dP*/*dT* calculated at 100ºC, which yields $P = 1.70$ atm	−1 point
Neglected units, which caused a numerical error	−2 to −4 points

5. Write the moles present in terms of the extent of reaction.

$$\begin{array}{ccccc} Cl_2CO & \leftrightarrow & Cl_2 & + & CO \\ 1-\xi & & \xi & & \xi \end{array}$$

The total number of moles present after ξ moles have reacted is $(1-\xi)+\xi+\xi = 1+\xi$. The partial pressures of the reactants and products are the mole fractions times the total pressure P_{total}.

$$P_{Cl_2CO} = \frac{1-\xi}{1+\xi}P_{\text{total}} \qquad P_{Cl_2} = \frac{\xi}{1+\xi}P_{\text{total}} \qquad P_{CO} = \frac{\xi}{1+\xi}P_{\text{total}}$$

Assume the gases are ideal, thus the activities equal the partial pressures divided by P^0 (= 1 bar.) The equilibrium constant is therefore

$$K_P = \frac{a_{Cl_2}a_{CO}}{a_{Cl_2CO}} \approx \frac{\frac{P_{Cl_2}}{P^0}\frac{P_{CO}}{P^0}}{\frac{P_{Cl_2CO}}{P^0}} = \frac{\frac{\xi}{1+\xi}P_{\text{total}}\frac{\xi}{1+\xi}P_{\text{total}}}{\frac{1-\xi}{1+\xi}P_{\text{total}}}\frac{1}{P^0} = \frac{\xi^2}{(1+\xi)(1-\xi)}\frac{P_{\text{total}}}{P^0} = \frac{\xi^2}{1-\xi^2}\frac{P_{\text{total}}}{P^0}$$

Substitute the extent of reaction and total pressure.

$$K_P = \frac{\xi^2}{1-\xi^2}\frac{P_{\text{total}}}{P^0} = \frac{(6.3\times10^{-5})^2}{1-(6.3\times10^{-5})^2}\frac{2\text{ bar}}{1\text{ bar}} = 7.94\times10^{-9}$$

Calculate $\Delta\overline{G}^0_{\text{rxn}}$.

$$\Delta\overline{G}^0_{\text{rxn}} = -RT\ln K_P = -(8.314\text{ kJ/K}\cdot\text{mol})(373\text{ K})\ln(7.94\times10^{-9}) = +57.8\text{ kJ/mol}$$

Grading Rubric:

Omitted key assumption; ideal gas so $a_i \approx P_i/P^0$	−1 point
Omitted factor of $1/P^0$ in K_P or K_P was not dimensionless	−1 point
Math error(s)	−1 to −3 points
Insignificant figures	−1 point