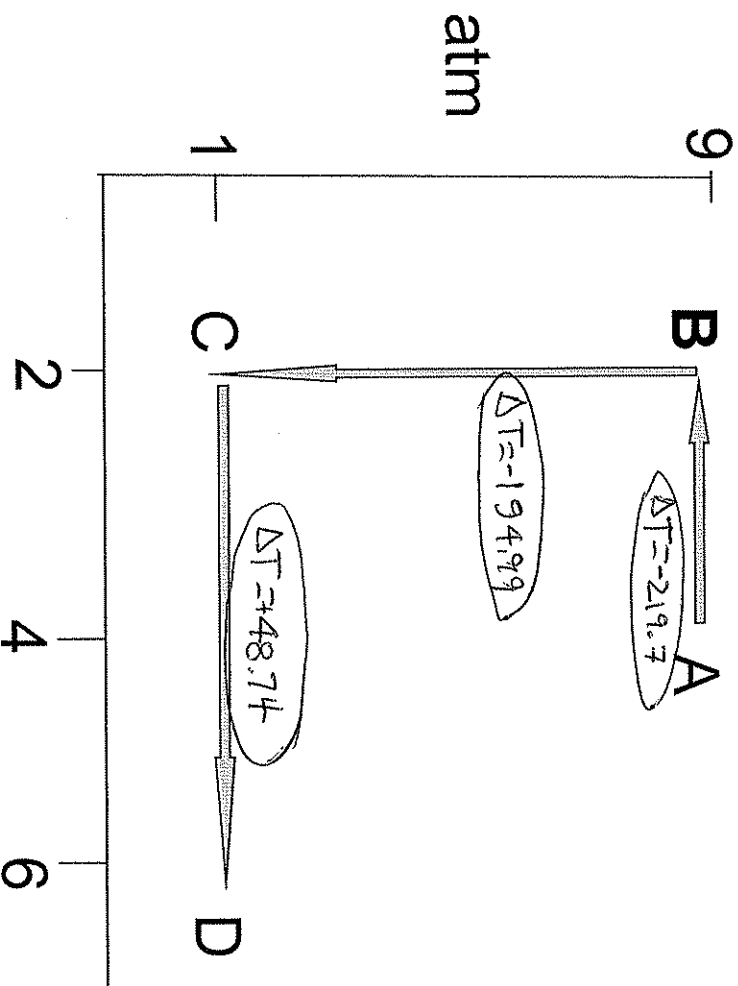


	ΔU	W	Q
	$\Delta U = nC_v \Delta T$	$w = \int p dV$	$Q = \Delta U - w$
A \Rightarrow B	$\frac{5}{2}R(219.37 - 438.74)$ - 4559.6	constant p; $w = p \Delta V$ $w = -9.1(2-4) = +18.2$ $+1823.85 J$	$-4559.6 - 1823.85 = -6383.4$ $C_p \Delta T = (\frac{7}{2}R) \Delta T = 6383.4 J$
B \Rightarrow C	$\frac{5}{2}R(24.38 - 219.37)$ - 4052.8	$w = 0$ constant V 0 J	- 4052.8 J
C \Rightarrow D	$\frac{5}{2}R(73.12 - 24.38)$ + 1013.1	constant p $w = -p \Delta V$ $w = -1(6-2) = -4$ $-405.3 J$	$C_p \Delta T = (\frac{7}{2}R) \Delta T = 1418.3 J$
Total	- 7599.3 J	+ 1418.55 J	- 9017.85



$$T_A = \frac{P_A V_A}{n_A R} = \frac{(101.325)A}{n_A R} = 438.74 K$$

$$T_B = 219.37 K$$

Temperature at C 24.38

Temperature at D 73.12 K

Volume (L)

ONE mole of O₂ gas (assume ideal gas) is introduced into a 4L vessel at a Pressure of 9 atm. Describe the changes in work, heat and internal energy as it moves through B, C and then D in REVERSIBLE processes. (15pts)

	ΔU	W	Q	ΔH	ΔS
	$\Delta U = nC_V \Delta T$	$W = -\int P dV$	$Q = \Delta U - W$	$\Delta H = nC_P \Delta T$	$nC_V \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{V_2}{V_1}\right)$
$D \Rightarrow A$	$\frac{5}{2} R (182.81) \times 2$ $+ 7599.4 J$	$\int_4^6 (-4V + 25) dV$ $= 1013.25 J$ <i>Wab, wbc, wcd same as D</i>	$6586.16 J$	$2 \times \left(\frac{7}{2}\right) R \times 182.81$ $10639.18 J$	$67.74 J$
Total	0	$2431.8 J$	$-2431.8 J$	0	0

$$\Delta S = 2 \left(\frac{5}{2} \right) R \ln \frac{219.37}{36.56} + 2.8314 \ln \left(\frac{4}{6} \right)$$

$$74.48 - 6.74 = 67.74 J$$

OR simply "add up squares"

$$101.35 (2 \times 8 + \frac{1}{2} (2 \times 8))$$

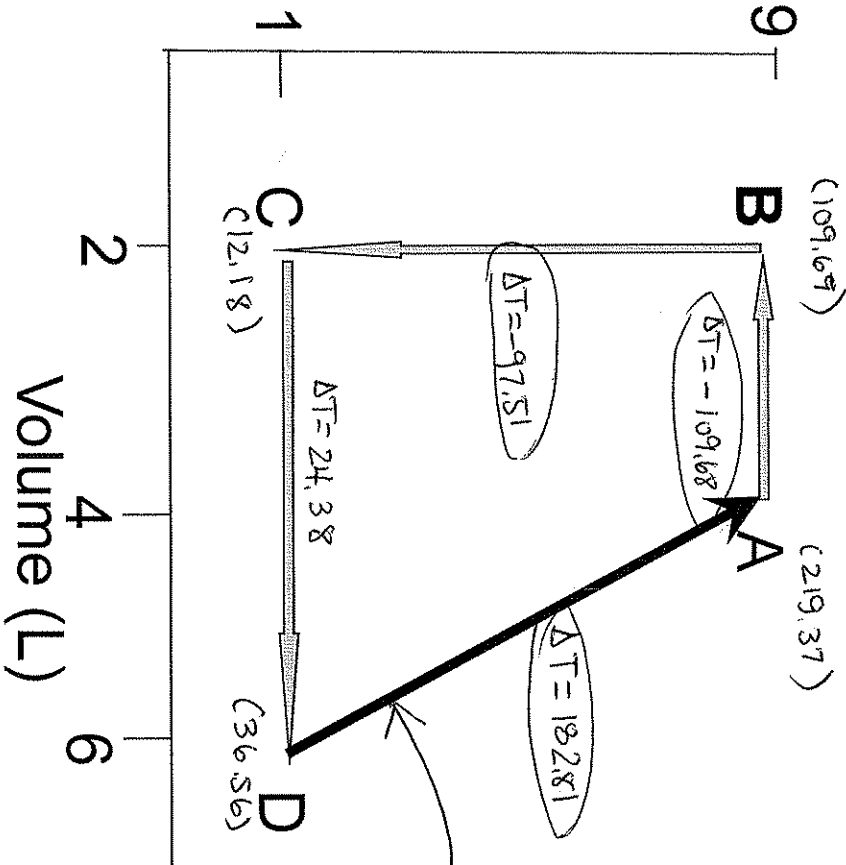
$$101.35 (24) = 2431.85$$

OR $\Delta H = \Delta U + [P_2 V_2 - P_1 V_1]$

$$7599.4 + 101.325 (9.4 - 6.1)$$

$$= 10639.15 J$$

atm



Temperature at A 219.37

$$T_A = \frac{P_A V_A}{nR} = \frac{9.4 \times 101.325}{2.8314}$$

$$P = -4V + 25 = \frac{9-1}{4-6} V + 6$$

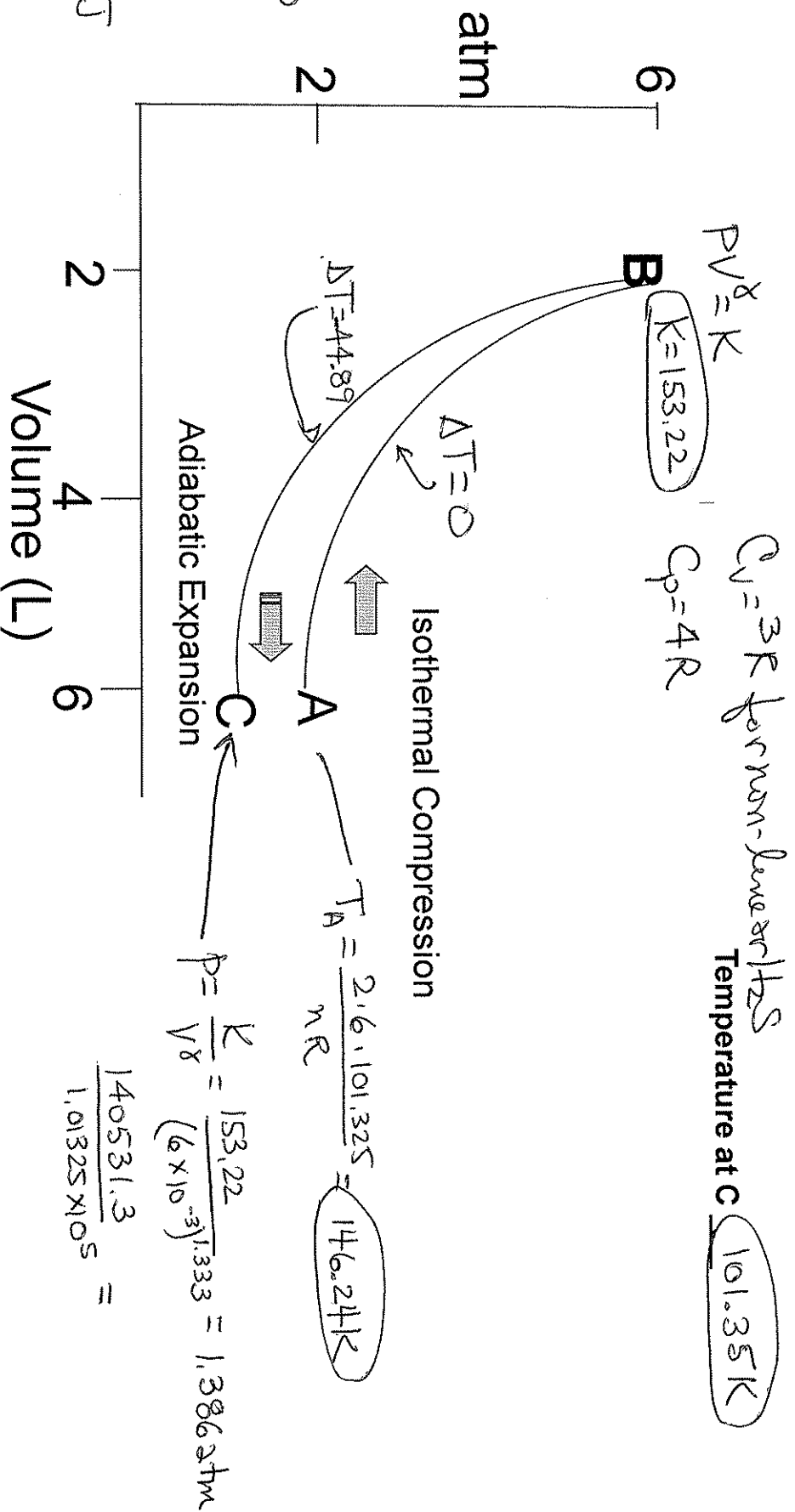
$$W = - \int_6^4 (-4V + 25) dV = - \left(-\frac{4V^2}{2} + 25V \right) \Big|_6^4$$

$$-68 - (-78) = +10$$

$$W = 10 \times 101.325 = 1013.25$$

TWO mole of O_2 gas (assume ideal gas) are introduced into a 4L vessel at 9atm (Point A) Describe the changes in work, heat and internal energy, Enthalpy and Entropy as it moves through the cycle in REVERSIBLE processes. (15pts)

	ΔU $n C_V \Delta T$	$W = - \int P_{\text{ext}} dV$	Q $Q = \Delta U - W$
A \Rightarrow B	Same T $\Delta T = 0$ $\Delta U = 0$	isotherm $- nRT \ln(V_2/V_1)$ $= +1335.7 \text{ J}$	-1335.7 J
B \Rightarrow C	$\Delta U = (1)(3R)(\Delta T)$ -1119.65 J	$w = \Delta U$ $= -1119.65 \text{ J}$	by definition
Total	-1119.65 J	216.05 J	-1335.7 J



One mole of H_2S gas (assume ideal gas) is introduced into a 6L vessel at 2 atm (Point A). Describe the changes in work, heat and internal energy as it moves through B, C in REVERSIBLE processes. (15pts)

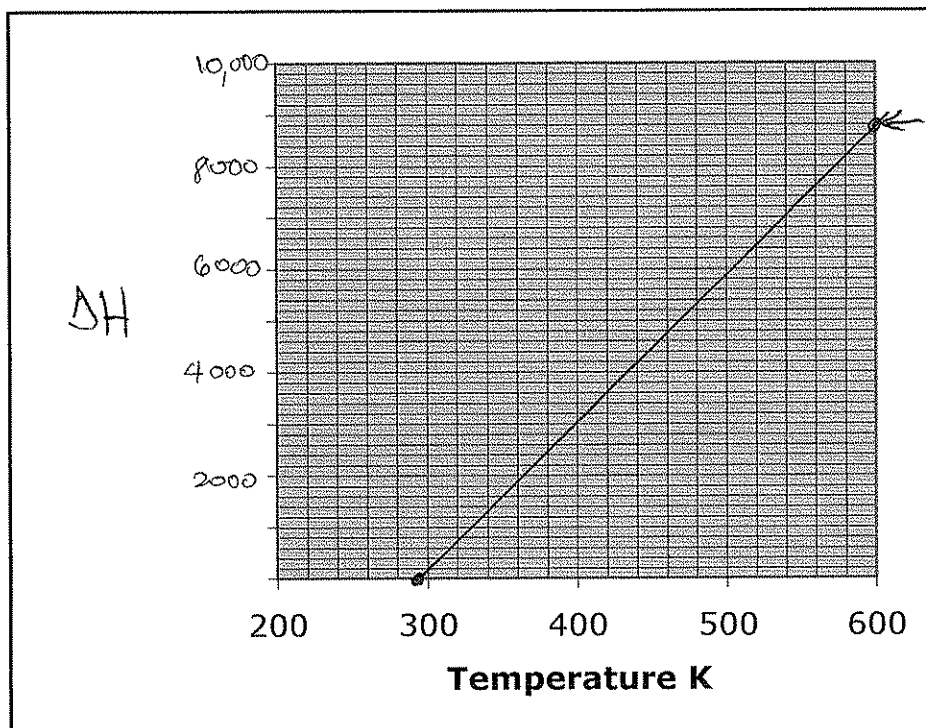
PROBLEM SET 3:

DO ANY SIX(6) of the next 10 Problems,
The FIRST 6 will be graded only!

3.1) The Temperature dependence of the molar heat capacity for $N_2(g)$

$$C_p \text{ (Joule/(K}\cdot\text{mole))} = 26.98 + 5.91E-03 T - 3.38E-07 T^2$$

Draw a reasonable graph of the temperature dependence of the Enthalpy of N_2 as a function of Temperature from RT to 600K (10pts) (Remember to add scale to the ordinate)



$$\Delta H = \Delta H_{298}^{\circ} + \int_{298}^T C_p dT = 0 + aT + \frac{bT^2}{2} + \frac{cT^3}{3} \Bigg|_{298}^T$$

T	$26.98T$	$\frac{5.91E-3T^2}{2}$	$-\frac{3.38E-7T^3}{3}$	
298	8040	262.4	-2.98	(8300)
400	10792	472.8	-7.21	(11,258)
600	16188	1063.8	-2434	(17,227)

$$\int_{298}^{400} = (11258 - 8300) = 2958 \text{ J} \quad \int_{298}^{600} = (17,227 - 8300) = 8927 \text{ J}$$

3.2) Two compartments of a cylinder are separated by a **movable piston** and their initial volumes are equal 450 and 100 cm³. The piston does **not conduct heat**. The initial temperature of a **DIATOMIC IDEAL gas** in the cylinder is 350 K and the pressure is 100 000 Pa. The gas in the first compartment is cooled down to 273 K and the gas in the second compartment is heated up to 473 K. What is the final pressure in the system? (10pts)

$$\begin{array}{ll} V = 100 \text{ cc} - V & 450 + V \\ T = 273 & 473 \\ n = 3.44 \times 10^{-3} & 1.55 \times 10^{-2} \end{array}$$

$$P_a = P_b$$

$$\frac{(3.44 \times 10^{-3}) R (273)}{100 - V} = \frac{1.55 \times 10^{-2} R (473)}{450 + V}$$

$$0.939(450 + V) = 7.3315(100 - V)$$

$$8.2705V = 310.7$$

$$V = 37.55 \rightarrow \boxed{P = 125025 \text{ Pa}}$$

If you worked the other problem

$$\begin{array}{ll} V = 100 + X & 473 - X \\ 473 & 273 \end{array}$$

$$\underbrace{\hspace{10em}}$$

$$V = 53.05$$

$$\boxed{P = 88,517 \text{ Pa}}$$

OR

3.3) For the ABOVE PROBLEM, how much heat in joules must be added or removed from these compartments to achieve the above final conditions. Can you thus determine the amount of work resulting in this process if it were conducted reversibly? (10pts)

Possible if one defines the "reversible" (slow) process by which initial $p, V \rightarrow p_f, V_f$. If you give me the surface/curve, I can integrate to get w and getting ΔU 's for both cells one can get Q 's!!

3.4) Calculate the work involved when one mole of an ideal gas is compressed reversibly from 45 cm^3 to 20 cm^3 at a constant temperature of 300K ? (10pts)

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

$$= (-)(8.314)(300) \ln\left(\frac{20}{45}\right) = \boxed{2022.6 \text{ J}}$$

3.5) How much energy as heat is required to raise the temperature of 2.00 moles of O_2 from 350°F to 550°F at 1.0 bar using the following relationship: (10pts)

$$\bar{C}_p[\text{O}_2(\text{g})]/R = 3.094 + (1.561 \times 10^{-3} \text{ K}^{-1})T - (4.65 \times 10^{-7} \text{ K}^{-2})T^2$$

$$\Delta H = 2 \times \int_{449.8 \text{ K}}^{560.93 \text{ K}} 25.7235 + 0.012978T - 3.866 \times 10^{-6}T^2$$

$$= 2 \times \left(25.7235T + \frac{0.012978T^2}{2} - \frac{3.866 \times 10^{-6}T^3}{3} \right) \Bigg|_{449.8}^{560.93}$$

$$2 [14,429 + 2040 - 227] - (11570 + 1310 - 117)$$

$$= 2 \times 3476.8 = \boxed{6953.6 \text{ Joules}}$$

3.6) Derive the relationship between C_p and C_v

For an IDEAL GAS, (5pts)

$$du = dq + dw \text{ @ Constant } V \quad \left(\frac{dq}{dT}\right)_v = \left(\frac{du}{dT}\right)_v = nC_v$$

At Constant Pressure

$$dq = du + p dV$$

$$p dV + V dp = nR dT \text{ for Ideal Gas}$$

but $V dp \rightarrow 0$ for constant p .

$$dq = du + nR dT$$

Differential with respect to T

$$\left(\frac{dq}{dT}\right)_p = nC_v \frac{dT}{dT} + nR \frac{dT}{dT} \Rightarrow nC_p = nC_v + nR$$

$$C_p = C_v + R$$

How would this relationship change if the gas were not ideal but rather

$$P(V-b) = nRT \text{ (5pts)}$$

If $p(V-b) = nRT$ then $p d(V-b) + p d(V-b) = nR dT$

$\rightarrow 0$ since constant p

and $d(V-b) = dV$ thus left unchanged

But if $a \neq 0$ for van der Waals.

$$\bar{C}_p - \bar{C}_v = \frac{R}{1 - \frac{2a}{RT} \cdot \frac{(V-b)^2}{V^3}}$$

3.7) A reaction involving ideal gases alone is found to be exothermic. As the reaction moves forward from only reactants, how would the equilibrium constant and subsequent rate alter. Consider the enthalpy, entropy and temperature dependence of each and their influence these results. Further discuss the difference $|Q-K|$ and rate would change. You must be thorough and support all comments based on theoretical and mathematical concepts. (10pts)

$K = e^{\Delta S/R} e^{-\Delta H/RT}$ for fixed ΔS and ΔH this K_{eq} will DECREASE with increasing temperature. BUT both ΔS and ΔH are temperature dependent. Each COMPONENT will increase (ΔH and ΔS) but differences associated with reactions are more complex. More modes on product side will result in less exothermicity. Changes in ΔS also depend on structure differences (to be visited). As reaction Q approaches K_{eq} it will slow down and this might be enhanced if "end" comes towards Q !

3.8) Derive the Central Theorem of Thermodynamics and use it to derive the Entropy of an Ideal Gas. (10pts)

$$dU = dQ + dW \quad \text{where } dQ_R = TdS \text{ and } dW = -PdV$$

$$dU = TdS - PdV \quad \text{or} \quad \boxed{TdS = dU + PdV}$$

For Ideal Gas $C_v = \left(\frac{dU}{dT}\right)_V$ Thus

$$TdS + C_v dT + PdV \Rightarrow \frac{TdS}{T} = \frac{nC_v dT + nRT}{VT} dV$$

$$\int dS = nC_v \int \frac{dT}{T} + nR \int \frac{dV}{V} \Rightarrow \boxed{\Delta S = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}}$$

3.9) Derive a kinetic relationship for the following a third order rate law where $R = k[X]^3$

Where the initial concentration of X is X_0 : (10pts)

$$\frac{d[X]}{dt} = -k[X]^3 \Rightarrow \int \frac{d[X]}{[X]^3} = -k \int dt \Rightarrow \left[\frac{X^{-2}}{-2} \right]_{X_0}^X = -kt \Big|_0^t$$

$$\boxed{\frac{1}{[X_0]^2} - \frac{1}{[X]^2} = 2kt}$$

3.10) More Difficult Problem: (10pts)

. Show that the work involved in a reversible, adiabatic pressure change of one mole of an ideal gas is given by

$$w = \bar{C}_v T_1 \left[\left(\frac{P_2}{P_1} \right)^{R/\bar{C}_p} - 1 \right]$$

where T_1 is the initial temperature and P_1 and P_2 are the initial and final pressures, respectively.

For an adiabatic expansion $\delta q = 0$, so $dU = \delta w$. By definition, $dU = n\bar{C}_v dT$, and for an ideal gas (Equation 19.2)

$$\delta w = -PdV = -nRTV^{-1}dV$$

We can then write

$$\begin{aligned} n\bar{C}_v dT &= -nRTV^{-1}dV \\ \int \frac{\bar{C}_v}{T} dT &= \int -\frac{R}{V} dV \\ \bar{C}_v \ln \left(\frac{T_2}{T_1} \right) &= -R \ln \left(\frac{V_2}{V_1} \right) \\ \ln \left(\frac{T_2}{T_1} \right)^{\bar{C}_v} &= \ln \left(\frac{V_2}{V_1} \right)^{-R} \end{aligned}$$

Finally, exponentiating both sides gives

$$\frac{T_2}{T_1} = \left(\frac{V_2}{V_1} \right)^{-R/\bar{C}_v} = \left(\frac{V_1}{V_2} \right)^{R/\bar{C}_v}$$