

EXAMPLE:

1. Given: The compressibility factor for a gas at 20°C is described by this equation for pressures up to 10 atm:

$$Z = 1 - 2.024 \times 10^{-2} p \quad \text{with } p \text{ in atm}$$

The following properties of this gas are also known:

$$C_V = 2.97 + 10.5 \times 10^{-3} T \quad \text{cal K}^{-1} \text{mol}^{-1}$$

$$C_p = 5.65 + 11.44 \times 10^{-3} T \quad \text{cal K}^{-1} \text{mol}^{-1}$$

$$(\partial U / \partial V)_T = 2 \times 10^{-3} \quad \text{cal L}^{-1}$$

2.0 moles of this gas undergoes a reversible isothermal expansion at 20°C from 8.0 atm to 1.0 atm.

Calculate V_i , V_f , W , ΔU , q , ΔH .

EXAMPLE:

2. Given: One mole of a monatomic ideal gas is compressed adiabatically in a single stage with a constant opposing pressure equal to 10.0 atm. Initially the gas is at 27°C and 1.0 atm pressure. The final pressure is 10.0 atm.

Calculate the final temperature of the gas.

EXAMPLE:

3. Given: One mole of an ideal gas of $C_V = 5 \text{ cal mol}^{-1} \text{ K}^{-1}$, initially at 0°C and 1.0 atm pressure, is put through the following reversible cycle:

A: State 1 to state 2, heated at constant volume to twice the initial absolute temperature.

B: State 2 to state 3, expanded adiabatically until it is back to the initial temperature.

C: State 3 to state 1, compressed isothermally back to state 1.

Calculate q , W , ΔU , ΔH for steps A, B, and C.

EXAMPLE:

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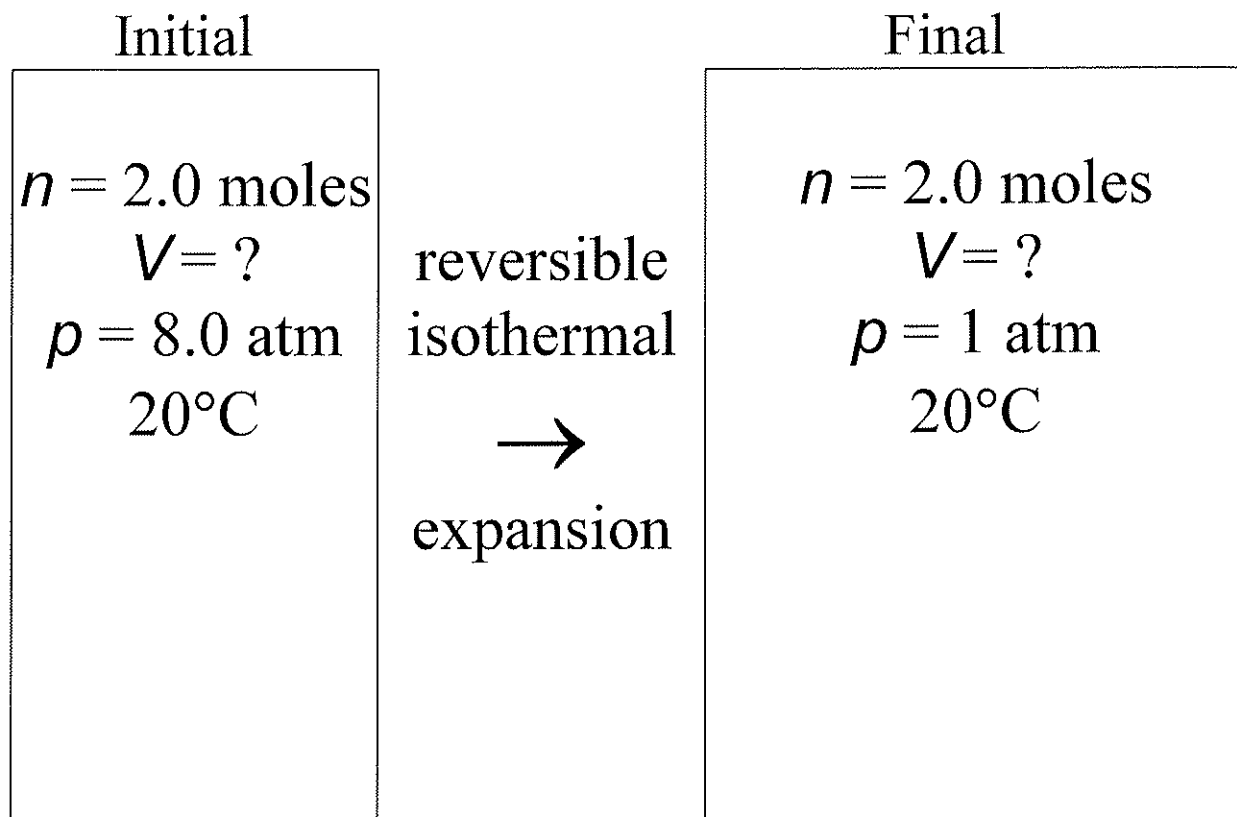
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2.0 moles of this gas undergoes a reversible isothermal expansion at 20°C from 8.0 atm to 1.0 atm.

Calculate V_i , V_f , W , ΔU , q , ΔH .

Draw a Picture:



Properties of the gas:

$$Z = pV/nRT = 1 - 2.024 \times 10^{-2} p \quad (p \text{ in atm})$$

for 20°C , up to 10 atm

$$C_V = 2.97 + 10.5 \times 10^{-3} T \text{ cal K}^{-1} \text{ mol}^{-1}$$

$$C_p = 5.65 + 11.44 \times 10^{-3} T \text{ cal K}^{-1} \text{ mol}^{-1}$$

$$(\partial U / \partial V)_T = 2 \times 10^{-3} \text{ cal L}^{-1}$$

Question: Calculate V_i , V_f , W , ΔU , q , ΔH .

Principles and Definitions involved:

isothermal $dT = 0$

reversible $p_{\text{op}} = p_{\text{gas}}$
 $\delta W = -p_{\text{op}} dV$

The first law: $d\mathbf{U} = \delta q + \delta W$

$$d\mathbf{U} = (\partial \mathbf{U} / \partial T)_V dT + (\partial \mathbf{U} / \partial V)_T dV$$

$$d\mathbf{H} = (\partial \mathbf{H} / \partial T)_p dT + (\partial \mathbf{H} / \partial p)_T dp$$

$$C_V = (\partial \mathbf{U} / \partial T)_V \quad C_p = (\partial \mathbf{H} / \partial T)_p$$

Solution:

Given the equation of state,

rearrange $pV/nRT = 1 - 2.024 \times 10^{-2} p$ to

$$V = nRT \left\{ (1/p) - 2.024 \times 10^{-2} \right\}$$

can solve for V , given T and p

$$V_i = \dots \text{ L}, \quad V_f = \dots \text{ L}$$

using $R = 8.20578 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}$

$$\delta W = -p_{op} dV$$

reversible, $\therefore p_{op} = p_{gas}$

$$W = - \int p_{gas} dV$$

$$= - \int \{ nRT / (nRT \cdot 2.024 \times 10^{-2} + V) \} dV$$

$$W = - 2R \cdot 293 \int dV / (2R \times 293 \times 2.024 \times 10^{-2} + V)$$

$$= - 2R \cdot 293 \times \ln \left[\frac{\{ 2R \times 293 \times 2.024 \times 10^{-2} + V_2 \}}{\{ 2R \times 293 \times 2.024 \times 10^{-2} + V_1 \}} \right]$$

$$R = 0.082057 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

$$W = \dots \text{ L atm}$$

$$\Delta U: \quad dU = C_V dT + (\partial U / \partial V)_T dV$$

$$\text{isothermal, } \therefore dT = 0 \quad \Delta U = \int (\partial U / \partial V)_T dV$$

$$\text{Given, } (\partial U / \partial V)_T = 2 \times 10^{-3} \text{ cal L}^{-1},$$

$$\Delta U = \int 2 \times 10^{-3} dV$$

$$\Delta U = 2 \times 10^{-3} (V_2 - V_1) \text{ cal}$$

$$q: \quad \text{First law, } \Delta U = q + W$$

Change W to cal by multiplying by

$$\{ 1.98718 \text{ cal} / 0.082057 \text{ L atm} \},$$

$$q = \dots \text{ cal}$$

$$\Delta H : \quad dH = C_p dT + (\partial H / \partial p)_T dp$$

$$\text{isothermal, } \therefore dT = 0 \quad \Delta H = \int (\partial H / \partial p)_T dp$$

$$(\partial H / \partial p)_T = [p + (\partial U / \partial V)_T] (\partial V / \partial p)_T + V$$

$$\text{Given: } V = nRT \{ (1/p) - 2.024 \times 10^{-2} \},$$

which differentiates to

$$(\partial V / \partial p)_T = -nRT p^{-2}$$

$$\text{Given, } (\partial U / \partial V)_T = 2 \times 10^{-3} \text{ cal L}^{-1}, \text{ convert to atm by} \\ \times \{ 0.082057 \text{ L atm} / 1.98718 \text{ cal} \}$$

$$\therefore (\partial H / \partial p)_T =$$

$$[p + 2 \times 10^{-3} (0.082057 / 1.98718)] \times -nRT p^{-2} + V$$

$$= -nRT \{ p^{-1} + 2 \times 10^{-3} (0.082057 / 1.98718) p^{-2} \} +$$

$$nRT \{ p^{-1} - 2.024 \times 10^{-2} \}$$

$$= -nRT \{ 2 \times 10^{-3} (0.082057 / 1.98718) p^{-2} + 2.024 \times 10^{-2} \}$$

$$\Delta H = \int (\partial H / \partial p)_T dp$$

$$= -nRT \int \{ 8.2586 \times 10^{-5} p^{-2} + 2.024 \times 10^{-2} \} dp$$

$$= nRT \{ 8.2586 \times 10^{-5} [p^{-1}]_8^1 + 2.024 \times 10^{-2} [1-8] \}$$

$$= nRT \{ 8.2586 \times 10^{-5} \times 7/8 + 2.024 \times 10^{-2} \times 7 \}$$

$$= nRT \times 2.024 \times 10^{-2} \times 7$$

$$= 2 \times 293 \times 1.987 \times 2.024 \times 10^{-2} \times 7 \text{ cal or}$$

$$= 2 \times 293 \times 8.3144 \times 2.024 \times 10^{-2} \times 7 \text{ joule}$$

EXAMPLE:

2. Given: One mole of a monatomic ideal gas is compressed adiabatically in a single stage with a constant opposing pressure equal to 10.0 atm. Initially the gas is at 27°C and 1.0 atm pressure. The final pressure is 10.0 atm. ***Calculate the final temperature of the gas.***

Draw a Picture:

Initial

$$n = 1 \text{ mole}$$

$$V = ?$$

$$p = 1 \text{ atm}$$

$$27^\circ\text{C}$$

monatomic
ideal gas

adiabatic

$$p_{op} = 10$$



compression

Final

$$n = 1 \text{ mole}$$

$$V = ?$$

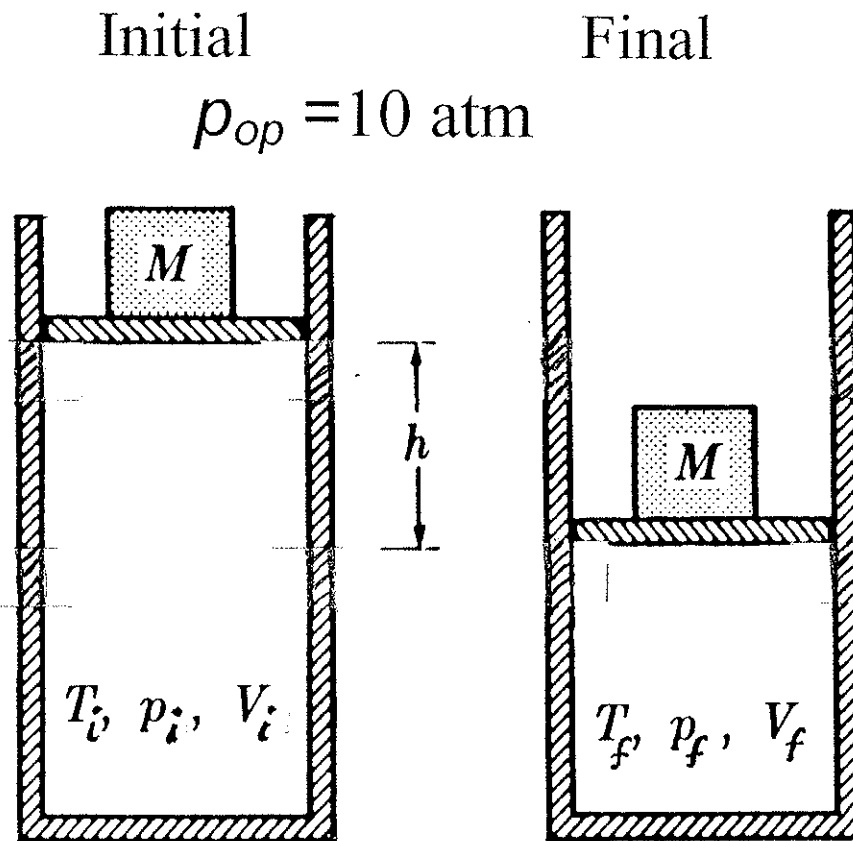
$$p = 10 \text{ atm}$$

$$T = ?$$

Question:

$$T_f = ?$$

Draw a Picture:



adiabatic compression
monatomic ideal gas

$n = 1 \text{ mole}$

$p_i = 1 \text{ atm}$

$T_i = 27 + 273.15$

$V_i = ?$

$n = 1 \text{ mole}$

$p_f = 10 \text{ atm}$

$T_f =$

$V_f = ?$

Question:

$T_f = ?$

Principles and Definitions involved:

adiabatic $\therefore q = 0$

$$\delta W = -p_{\text{op}} dV$$

The first law: $dU = \delta q + \delta W$

$$dU = (\partial U / \partial T)_V dT + (\partial U / \partial V)_T dV$$

$$C_V = (\partial U / \partial T)_V$$

Ideal gas: $pV = nRT$ $(\partial U / \partial V)_T = 0$

monatomic: $C_V = (3/2)R$

Solution:

$$pV = nRT$$

using $R = 8.20578 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}$

$$\begin{aligned} V_i &= 1.0 \text{ mol} \times R \times 300 \text{ K} / 1.0 \text{ atm} \\ &= 300R \text{ L} \end{aligned}$$

$$\begin{aligned} V_f &= 1.0 \text{ mol} \times R \times T_f \text{ K} / 10. \text{ atm} \\ &= RT_f / 10 \text{ L} \end{aligned}$$

{ Can not get T_f from equation of state alone. Need to use the fact that the process is adiabatic. }

$$q: \quad q = 0 \quad \text{adiabatic}$$

$$W: \quad \delta W = - p_{op} dV \quad p_{op} = 10 \text{ atm}$$

$$W = - \int_{V_i}^{V_f} 10 dV = -10[V_f - V_i]$$

$$= -10 [RT_f/10 - 300 R]$$

$$\Delta U: \quad dU = C_V dT + (\partial U / \partial V)_T dV$$

for an ideal gas only, $(\partial U / \partial V)_T = 0$

$$\therefore \Delta U = \int C_V dT + 0 \quad C_V = (3/2)R \text{ (monatomic)}$$

$$\Delta U = \int_{300}^{T_f} (3/2)R dT = (3/2)R [T_f - 300]$$

$$\text{First law:} \quad \Delta U = q + W$$

$$(3/2)R [T_f - 300] = 0 + -10R [T_f/10 - 300]$$

Solve for T_f

EXAMPLE:

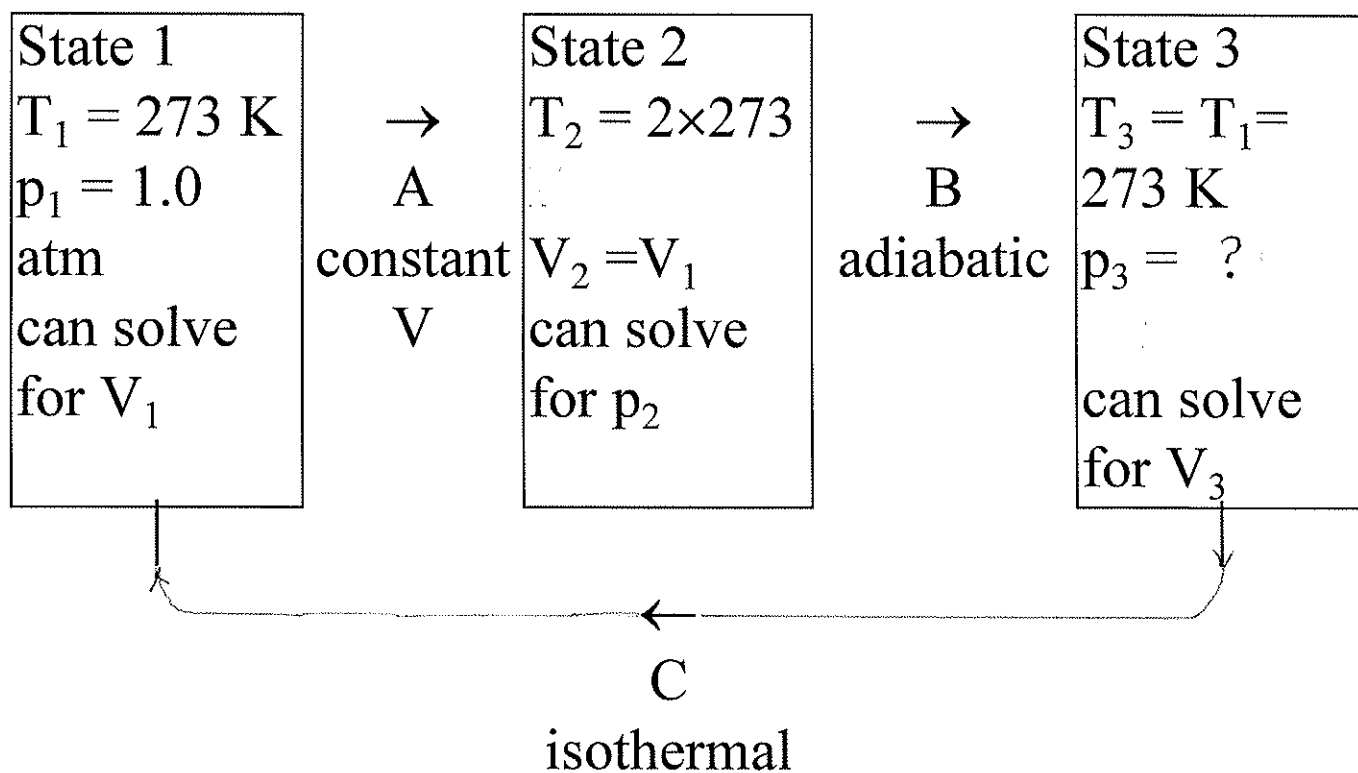
3. Given: One mole of an ideal gas of $C_V = 5 \text{ cal mol}^{-1} \text{ K}^{-1}$, initially at 0°C and 1.0 atm pressure, is put through the following reversible cycle:

A: State 1 to state 2, heated at constant volume to twice the initial absolute temperature.

B: State 2 to state 3, expanded adiabatically until it is back to the initial temperature.

C: State 3 to state 1, compressed isothermally back to state 1.

Calculate q , W , ΔU , ΔH for steps A, B, and C.



Principles and Definitions involved:

$$\delta W = - p_{\text{op}} dV$$

The first law: $d\mathbf{U} = \delta q + \delta W$

$$d\mathbf{U} = (\partial \mathbf{U} / \partial T)_V dT + (\partial \mathbf{U} / \partial V)_T dV$$

$$d\mathbf{H} = (\partial \mathbf{H} / \partial T)_p dT + (\partial \mathbf{H} / \partial p)_T dp$$

$$C_V = (\partial \mathbf{U} / \partial T)_V \quad C_p = (\partial \mathbf{H} / \partial T)_p$$

Ideal gas: $pV = nRT \quad (\partial \mathbf{U} / \partial V)_T = 0$

$$C_p - C_V = R \quad (\partial \mathbf{H} / \partial p)_T = 0$$

reversible $p_{\text{op}} = p_{\text{gas}}$

Step A: constant volume $dV = 0$

Step B: adiabatic $q = 0$

Step C: isothermal $dT = 0$

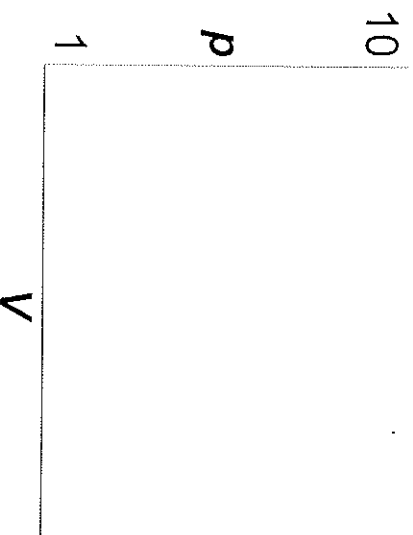
$C_V = 5.0 \text{ cal mol}^{-1} \text{ K}^{-1}$, ideal gas, $C_p - C_V = R$, $\therefore C_p = 7 \text{ cal mol}^{-1} \text{ K}^{-1}$

A reversible constant V, $V_2 = V_1$	B reversible, adiabatic $T_3 = T_1$	C reversible isothermal T_1
$T_i = T_1 = 273 \text{ K}$ $T_f = T_2 = 2 \times 273 \text{ K}$ $p_1 = 1 \text{ atm}$, solve for V_1	$T_i = T_2 = 2 \times 273 \text{ K}$ $T_f = T_3 = 273 \text{ K}$	$T_i = T_3 = 273 \text{ K}$ $T_f = T_1 = 273 \text{ K}$ $p_3 = ?$, $V_3 = ?$
q : $\Delta U = q + W$ take $\Delta U, W$ from below or else $C_V \equiv \delta q_V / dT$ $q_V = \int C_V dT$	q : $q = 0$ (adiabatic) \therefore can solve for V_3 by $dU = \delta q + \delta W = 0 + \delta W$ $C_V dT = -p_{\text{gas}} dV$ $C_V dT/T = -R dV/V$ $5 \ln(T_3/T_2) = -R \ln(V_3/V_1)$	q : $\Delta U = q + W$ take $\Delta U, W$ from below
W $\delta W = -p_{\text{op}} dV$ given $dV = 0$, $\therefore W = 0$	W : $\Delta U = q + W$ $\Delta U = 0 + W$ take ΔU from below	W : $\delta W = -p_{\text{op}} dV$ $p_{\text{op}} = p_{\text{gas}}$ (reversible) $W = -\int (RT/V) dV$ $= -R 273 \ln(V_1/V_3)$
ΔU $dU = C_V dT$ $+ (\partial U / \partial V)_T dV$ ideal gas, $\therefore (\partial U / \partial V)_T = 0$ or given $dV = 0$, $\therefore \Delta U = \int C_V dT$	ΔU $dU = C_V dT$ $+ (\partial U / \partial V)_T dV$ as on the left $\Delta U = \int C_V dT$	ΔU $dU = C_V dT$ $+ (\partial U / \partial V)_T dV$ ideal gas, $\therefore (\partial U / \partial V)_T = 0$ and given $dT = 0$ $\therefore \Delta U = 0$
ΔH $dH = C_p dT$ $+ (\partial H / \partial p)_T dp$ ideal gas, $\therefore (\partial H / \partial p)_T = 0$ $\therefore \Delta H = \int C_p dT$	ΔH $dH = C_p dT$ $+ (\partial H / \partial p)_T dp$ as on the left $\Delta H = \int C_p dT$	ΔH $dH = C_p dT$ $+ (\partial H / \partial p)_T dp$ ideal gas, $\therefore (\partial H / \partial p)_T = 0$ given $dT = 0$, $\therefore \Delta H = 0$

EXAMPLE:

Assume that air behaves as an ideal gas with $C_p = (7/2)R$.

(a) In one experiment 1.00 mole of "air molecules" is compressed from 1.00 atm to 10.0 atm at 25°C by the following reversible process: (1) heating at constant volume to the final pressure followed by (2) cooling at constant pressure to 25°C. Sketch these processes on a pV diagram.



Calculate ΔU , ΔH , q , and W , in kJ for each step in the process and for the overall process.

EXAMPLE:

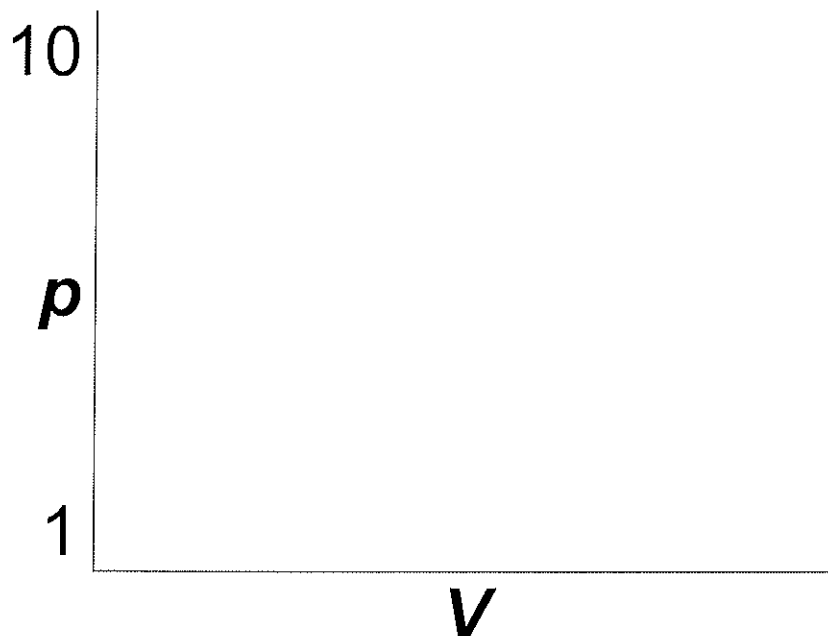
n moles of a gas obeying the eqn. of state $p(V-nb) = nRT$ where $b = 0.1 \text{ L mol}^{-1}$ and has $(\partial U / \partial V)_T = 0$, $(\partial H / \partial p)_T = -b$ is subjected to an isothermal reversible expansion from an initial volume of 1.00 L to 24.89 L at 298 K.

Calculate the values of ΔU , ΔH , q , and W , in kJ in terms of n .

EXAMPLE:

Assume that air behaves as an ideal gas with $C_p = (7/2)R$.

(a) In one experiment 1.00 mole of “air molecules” is compressed from 1.00 atm to 10.0 atm at 25°C by the following reversible process: (1) heating at constant volume to the final pressure followed by (2) cooling at constant pressure to 25°C. Sketch these processes on a pV diagram.



Calculate ΔU , ΔH , q , and W , in kJ for each step in the process and for the overall process.

Principles and equations for this problem:

Ideal gas, for which: $pV = nRT$ $(\partial U/\partial V)_T = 0$
 $(\partial H/\partial p)_T = 0$, $C_p - C_V = R$

$C_p = (7/2)R$, given

ideal gas $\therefore C_V = C_p - R = (5/2)R$

definition of heat capacity C : $q = \int C dT$

First law $\Delta U = q + W$

$$dW = -p_{op}dV$$

$$U(T, V) : dU = C_V dT + (\partial U/\partial V)_T dV$$

$$H(T, p) : dH = C_p dT + (\partial H/\partial p)_T dp$$

definition of ***reversible*** process: $p_{op} = p_{gas}$

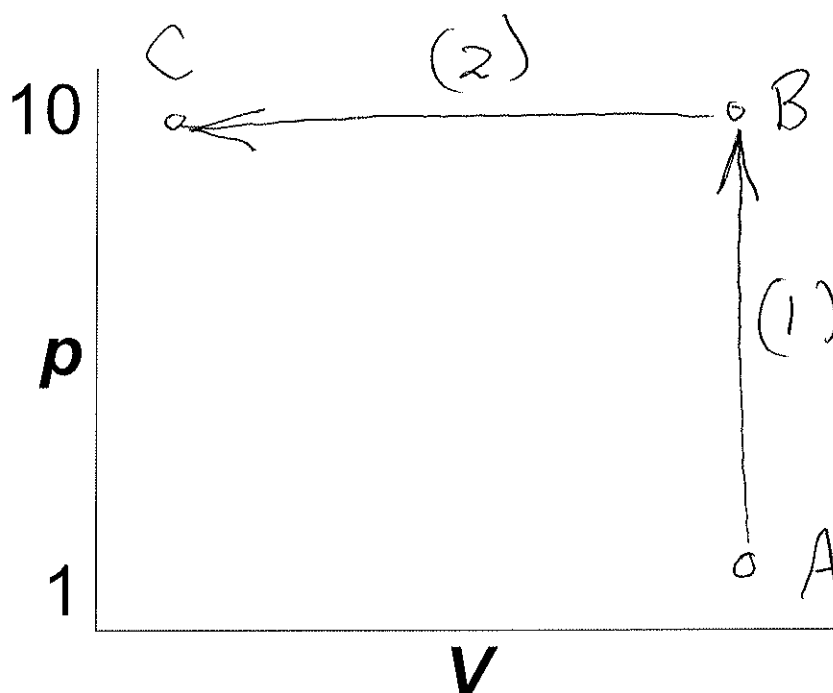
Solution:

step 1 $A \rightarrow B$ constant volume

step 2 $B \rightarrow C$ constant pressure

(state) _A	(state) _B	(state) _C
$p_A = 1$ given	$p_B = 10$ given	$p_C = 10$ given
$T_A = 298$ given	$T_B = 10V_A/R$	$T_C = 298$ given
$V_A = R \cdot 298/1$	$V_B = V_A$ given	$V_C = R \cdot 298/10$

$n=1$, p in atm, T in K, V in L



<i>step 1</i> $dV=0$	<i>step 2</i> $dp=0$	<i>overall= 1+2</i>
$\mathbf{q} = \mathbf{q}_V =$ $\int_{T_A}^{T_B} C_V dT =$ $(5/2)8.314[2980-298] = 55.748 \text{ kJ}$	$\mathbf{q} = \mathbf{q}_p =$ $\int_{T_B}^{T_C} C_p dT =$ $(7/2)8.314[298-2980] = -78.047 \text{ kJ}$	55.748 $+$ (-78.047) $= -22.3 \text{ kJ}$
$d\mathbf{W} = -\mathbf{p}_{op}dV$ $dV=0$ $\therefore \mathbf{W} = 0$	$\mathbf{W} = \Delta\mathbf{U} - \mathbf{q} =$ $-55.748 - (-78.047)$ $= +22.3 \text{ kJ}$	0 $+$ 22.3 kJ
$d\mathbf{U} = C_V dT$ $+ (\partial\mathbf{U}/\partial V)_T dV$ $dV=0$ $\Delta\mathbf{U} = \int_{T_A}^{T_B} C_V dT$	$d\mathbf{U} = C_V dT$ $+ (\partial\mathbf{U}/\partial V)_T dV$ $(\partial\mathbf{U}/\partial V)_T = 0$ $\Delta\mathbf{U} = \int_{T_B}^{T_C} C_V dT$ $= (5/2)8.314[298-2980] = -55.748 \text{ kJ}$	$\Delta\mathbf{U}=0$ since $T_C = T_A$ and ideal
$d\mathbf{H} = C_p dT$ $+ (\partial\mathbf{H}/\partial p)_T dp$ $(\partial\mathbf{H}/\partial p)_T = 0$ $\Delta\mathbf{H} = \int_{T_A}^{T_B} C_p dT$ $(7/2)8.314[2980-298] = 78.047 \text{ kJ}$	$d\mathbf{H} = C_p dT$ $+ (\partial\mathbf{H}/\partial p)_T dp$ $dp=0$ $\Delta\mathbf{H} = \int_{T_B}^{T_C} C_p dT$ $(7/2)8.314[298-2980] = -78.047 \text{ kJ}$	$\Delta\mathbf{H}=0$ since $T_C = T_A$ and ideal

Note that $dW = -p_{op}dV$ could also have been used for step 2, giving the same answer:

since $p_{op} = \text{constant} = 10 \text{ atm}$ in step 2,

$$\begin{aligned} W &= -10 \int_{V_B}^{V_C} dV \\ &= -10 \text{ atm} \int_{R298/1}^{R298/10} dV \\ &= -10 \left[\frac{R298}{10} - \frac{R298}{1} \right] \\ &= 220.077 \text{ L atm} \times \frac{0.0083144 \text{ kJ}}{0.082057 \text{ L atm}} \\ &= 22.3 \text{ kJ} \end{aligned}$$

EXAMPLE:

n moles of a gas obeying the eqn. of state
 $p(V-nb) = nRT$ where $b=0.1 \text{ L mol}^{-1}$

and has $(\partial \mathbf{U}/\partial V)_T = 0$, $(\partial \mathbf{H}/\partial p)_T = -b$

is subjected to an isothermal reversible
expansion from an initial volume of 1.00 L to
24.89 L at 298 K.

Calculate the values of $\Delta \mathbf{U}$, $\Delta \mathbf{H}$, q , and \mathbf{W} , in
kJ in terms of n .

Principles and equations for this problem:

First law $\Delta \mathbf{U} = \mathbf{q} + \mathbf{W}$

$$dW = -p_{op}dV$$

$$\mathbf{U}(T, V) : d\mathbf{U} = C_V dT + (\partial \mathbf{U} / \partial V)_T dV$$

$$\mathbf{H}(T, p) : d\mathbf{H} = C_p dT + (\partial \mathbf{H} / \partial p)_T dp$$

definition of **reversible** process: $p_{op} = p_{gas}$

definition of **isothermal** process: $T_{final} = T_{initial}$

Given:

eqn. of state: $p(V-nb) = nRT$ $b=0.1 \text{ L mol}^{-1}$

$$(\partial \mathbf{U} / \partial V)_T = 0, (\partial \mathbf{H} / \partial p)_T = -b$$

Solution:

(state) _{initial}	(state) _{final}
$T_i = 298 \text{ K}$ given	$T_f = 298 \text{ K}$ given
$V_i = 1 \text{ L}$ given	$V_f = 24.8 \text{ L}$ given
$p_i = \frac{nR298}{(1.0-0.1n)}$	$p_f = \frac{nR298}{(24.8-0.1n)}$

$$dW = -p_{op}dV \quad p_{op} = p_{gas}$$

$$W = -\int p_{gas}dV$$

$$= - \int_{V_i}^{V_f} \frac{nR \ 298}{V - nb} dV = -nR \ 298 \ln \left(\frac{24.8 - 0.1n}{1.0 - 0.1n} \right)$$

$$dU = C_V dT + (\partial U / \partial V)_T dV$$

$$dT = 0, \ (\partial U / \partial V)_T = 0 \text{ given}, \ \therefore \Delta U = 0$$

$$q = \Delta U - W = -W = nR \ 298 \ln \left(\frac{24.8 - 0.1n}{1.0 - 0.1n} \right)$$

$$dH = C_p dT + (\partial H / \partial p)_T dp$$

$$dT = 0, \ (\partial H / \partial p)_T = -b, \ \therefore \Delta H = \int (\partial H / \partial p)_T dp =$$
$$-b \int_{p_i}^{p_f} dp$$

$$= -0.1 \times n \times 0.0083144 \times 298 \left[\frac{1}{24.8 - 0.1n} - \frac{1}{1.0 - 0.1n} \right] \text{ kJ}$$

Chemistry 116

Quiz 1 on Chapter 7-8

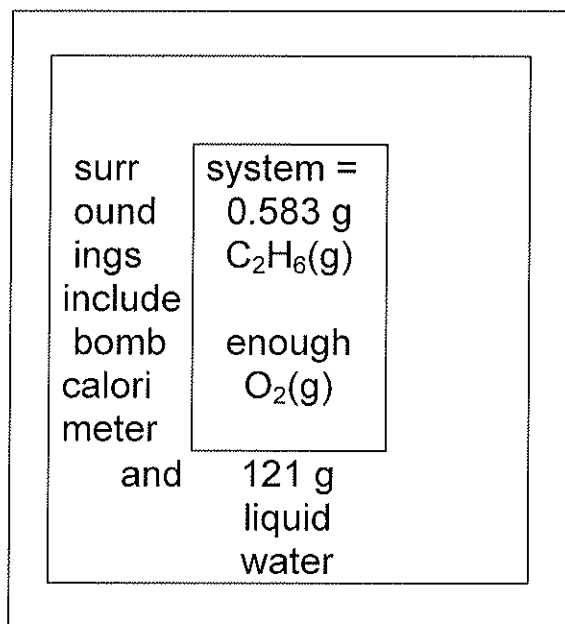
Name _____

Problem: A 0.583 g sample of $C_2H_6(g)$ is burned in a bomb calorimeter containing 121 g of water as the heat exchange substance. The temperature rises from 22.145 to 41.405 °C. Taking the heat capacity of the calorimeter to be 1.0489 kJ/°C calculate q_V the molar heat of combustion of $C_2H_6(g)$ at constant volume, in kJ mol⁻¹. What is ΔE for the combustion of C_2H_6 ? Assuming that the gases behaved ideally, what is ΔH_c for C_2H_6 ? The specific heat capacity of liquid water is 4.184 J g⁻¹/°C. $R = 8.31451 \text{ J K}^{-1} \text{ mol}^{-1}$

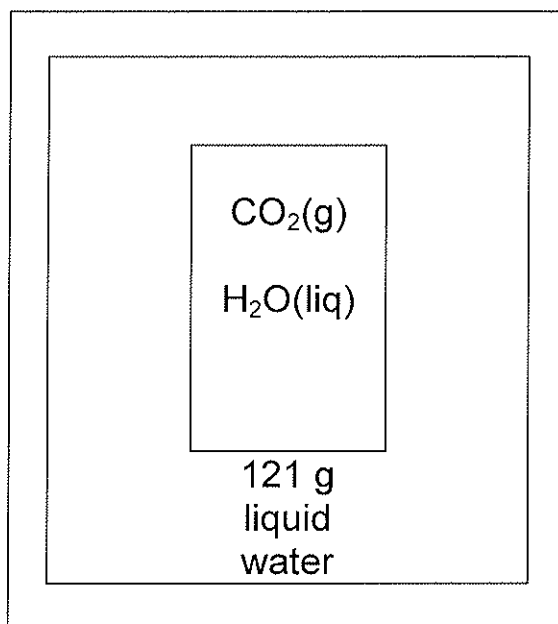
(1) Draw a picture

22.145
°C

41.405
°C



initial



final

(2) molar mass of C_2H_6 =
moles of $C_2H_6(g)$ =

_____ g mol⁻¹
_____ mol

(3) definition of heat capacity: $q = C \Delta T$
surroundings: $q_{surr} =$

_____ kJ

(4) $\therefore q_{system} = q_V =$ _____ kJ
molar heat of combustion of $C_2H_6(g)$ at constant volume, molar $q_V =$

(5) First law of thermodynamics leads to $\Delta E = q_V$ (general, when only
pressure volume work
is possible)

$\therefore \Delta E$ of combustion of $C_2H_6(g) =$ _____ kJ mol⁻¹.

(6) Definition of enthalpy: $H = E + pV$
Ideal gas equation of state: $pV = nRT$
The balanced chemical equation:

(neglect the volume occupied by the liquid water resulting from the combustion.)

For 1 mole of C_2H_6 :

gases initial: _____ gases final: _____.

calculate ΔH here:

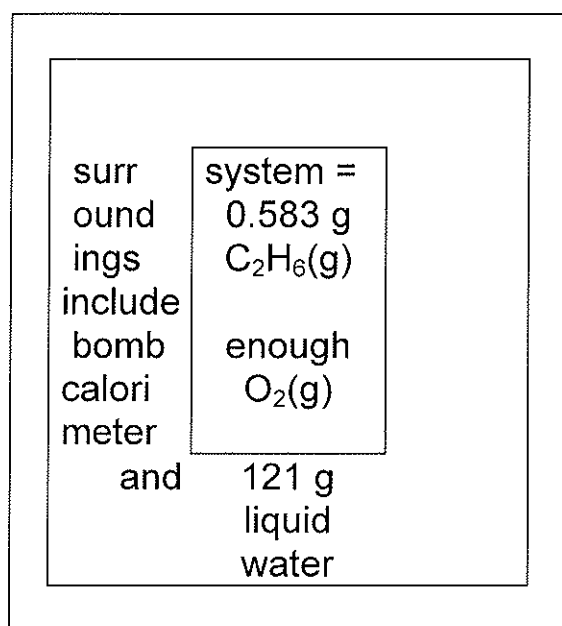
$\therefore \Delta H$ of combustion of $C_2H_6(g)$
= _____ kJ mol⁻¹

Problem: A 0.583 g sample of $\text{C}_2\text{H}_6(\text{g})$ is burned in a bomb calorimeter containing 121 g of water as the heat exchange substance. The temperature rises from 22.145 to 41.405 °C. Taking the heat capacity of the calorimeter to be 1.0489 kJ/°C calculate q_V the molar heat of combustion of $\text{C}_2\text{H}_6(\text{g})$ at constant volume, in kJ mol⁻¹. What is ΔE for the combustion of C_2H_6 ? Assuming that the gases behaved ideally, what is ΔH_c for C_2H_6 ? The specific heat capacity of liquid water is 4.184 J g⁻¹/°C. $R = 8.31451 \text{ J K}^{-1} \text{ mol}^{-1}$

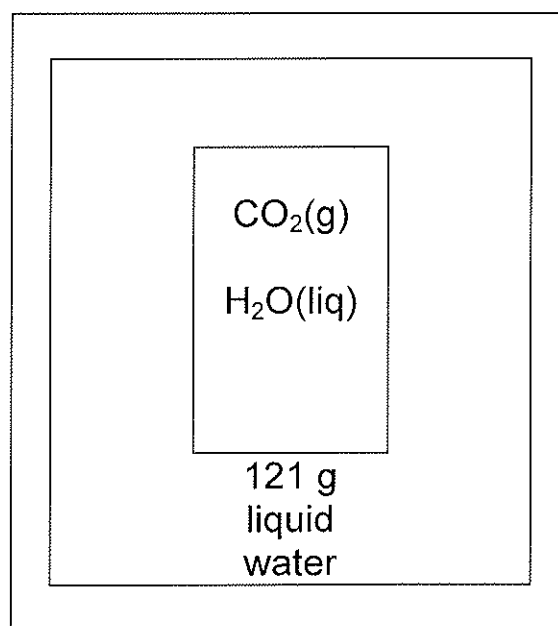
(1) Draw a picture

22.145
°C

41.405
°C



initial



final

(2) molar mass of $\text{C}_2\text{H}_6 = 2 \times 12 + 6 \times 1.008$
 moles of $\text{C}_2\text{H}_6(\text{g}) = 0.583 / 30.048 \text{ g mol}^{-1} = \frac{30.048 \text{ g mol}^{-1}}{0.0194 \text{ mol}}$

(3) definition of heat capacity: $q = C \Delta T$

surroundings: $q_{\text{surr}} = 1.0489 \text{ kJ/}^\circ\text{C} \times (41.405 - 22.145) ^\circ\text{C} +$
 $121 \text{ g} \times 4.184 \text{ J g}^{-1}/^\circ\text{C} \times (41.405 - 22.145) ^\circ\text{C} \times 10^{-3} \text{ kJ/J}$
 $= 20.202 \text{ kJ} + 9.751 \text{ kJ} =$

29.953 kJ

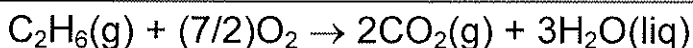
Note that heat is discovered in the surroundings (the temperature of the calorimeter and the water increased!) This means that heat flowed from the system to the surroundings. The system LOST heat. Therefore $q_{\text{system}} < 0$.

$$(4) \therefore q_{\text{system}} = q_V = -q_{\text{surr}} = \frac{-29.953 \text{ kJ}}{\text{molar heat of combustion of } \text{C}_2\text{H}_6(\text{g}) \text{ at constant volume, molar } q_V = -29.953 \text{ kJ}/0.0194 \text{ mol} =}$$

$$(5) \text{ First law of thermodynamics leads to } \Delta E = q_V \text{ (general, when only pressure volume work is possible)}$$

$$\therefore \Delta E \text{ of combustion of } \text{C}_2\text{H}_6(\text{g}) = \frac{-1543.97}{\text{kJ mol}^{-1}}.$$

(6) Definition of enthalpy: $H = E + pV$
 Ideal gas equation of state: $pV = nRT$
 The balanced chemical equation:



(neglect the volume occupied by the liquid water resulting from the combustion.)

For 1 mole of C_2H_6 :

gases initial: 1 mol $\text{C}_2\text{H}_6(\text{g}) + (7/2)$ mol $\text{O}_2(\text{g})$ gases final: 2 $\text{CO}_2(\text{g})$.

calculate ΔH here:

$$\begin{aligned} \Delta H &= \Delta E + (pV)_{\text{final}} - (pV)_{\text{initial}} = \Delta E + (nRT)_{\text{final}} - (nRT)_{\text{initial}} \\ &= -1543.97 \text{ kJ mol}^{-1} + 2R \times 314.56 \text{ K} - 4.5R \times 295.30 \text{ K} \\ &= -1543.97 \text{ kJ mol}^{-1} \\ &\quad + (2 \times 314.56 - 4.5 \times 295.30) \times 8.31451 \times 10^{-3} \text{ kJ mol}^{-1} \\ &= -1543.97 \text{ kJ mol}^{-1} - 699.73 \times 8.31451 \times 10^{-3} \text{ kJ mol}^{-1} \\ &= -1543.97 \text{ kJ mol}^{-1} - 5.818 \text{ kJ mol}^{-1} \end{aligned}$$

$$\therefore \Delta H \text{ of combustion of } \text{C}_2\text{H}_6(\text{g}) = \frac{-1549.79}{\text{kJ mol}^{-1}}$$