Clase 12 20 Agosto 2014

Título de la nota 21/08/2014

Proceso Adiabático Irreversible

$$\Delta U = Q - W$$

$$Q = 0$$

$$\Delta U = -W$$

$$W_{irrev} = p_2(V_2 - V_1)$$

$$\Delta U = n\bar{C}_v \Delta T$$

$$\Delta H = n\bar{C}_p \Delta T$$

} gas perfecto

$\bar{C}_p$ y $\bar{C}_v$ = ctes

si $\quad \Delta U = -W \qquad dU = -\delta W$

$$n\bar{C}_v \Delta T = -p\Delta V$$

$$n\bar{C}_v dT = -p\,dV \qquad p = p_2$$

$$n\bar{C}_v (T_2 - T_1) = -p_2 (V_2 - V_1)$$

$$n\bar{C}_v (T_2 - T_1) = -p_2 \left[\frac{nRT_2}{p_2} - \frac{nRT_1}{p_1} \right]$$ eliminando

$$n\bar{C}_v (T_2 - T_1) = p_2 \left[\frac{T_1}{p_1} R - \frac{R\,T_2}{p_2} \right]$$ Factorizando

$$\bar{C}_v (T_2 - T_1) = R \left[\frac{P_2 T_1}{P_1} - T_2 \right]$$

Agrupando

$$T_2 - T_1 = \frac{R}{\bar{C}_v} \left[\frac{P_2 T_1}{P_1} - T_2 \right]$$

$$T_2 = \frac{R}{\bar{C}_v} \left[\frac{P_2 T_1}{P_1} - T_2 \right] + T_1$$

$$T_2 = \frac{\bar{C}_p - \bar{C}_v}{\bar{C}_v} \left[\frac{P_2 T_1}{P_1} - T_2 \right] + T_1$$

$$T_2 = \gamma - 1 \left[\frac{p_2 T_1}{p_1} - T_2 \right] + T_1$$

$$T_2 + T_2(\gamma - 1) = \gamma - 1 \left[\frac{p_2}{p_1} T_1 \right] + T_1$$

$$T_2 + T_2\gamma - T_2 = T_1 \left[(\gamma - 1) \frac{p_2}{p_1} + 1 \right]$$

$$T_2 \gamma = T_1 \left[(\gamma - 1) \frac{p_2}{p_1} + 1 \right]$$

$$T_2 = \frac{T_1}{\gamma} \left[(\gamma - 1) \frac{p_2}{p_1} + 1 \right]$$

Obtención de la Relación V vs P

$$\frac{T_2}{T_1} = \frac{1}{\gamma}\left[(\gamma-1)\frac{P_2}{P_1} + 1\right]$$

Sustituyendo

$$\frac{P_2V_2/nR}{P_1V_1/nR} = \frac{1}{\gamma}\left[(\gamma-1)\frac{P_2}{P_1} + 1\right]$$

$$P_2V_2 = \frac{P_1V_1}{\gamma}\left[(\gamma-1)\frac{P_2}{P_1} + 1\right]$$

$$P_2V_2 = \left[\frac{P_1V_1}{\gamma}(\gamma-1)\frac{P_2}{P_1} + \frac{P_1V_1}{\gamma}\right]$$

eliminando

$$P_2V_2 = \left[\frac{V_1}{\gamma}(\gamma-1)P_2 + \frac{P_1V_1}{\gamma}\right]$$

$$p_2 V_2 \gamma = \left[(\gamma - 1) V_1 P_2 + P_1 V_1 \right]$$

$$p_2 V_2 \gamma = V_1 \left[(\gamma - 1) P_2 + P_1 \right]$$

$$p_2 V_2 = \frac{V_1}{\gamma} \left[(\gamma - 1) P_2 + P_1 \right]$$ dividiendo entre p_2

$$\frac{p_2 V_2}{P_2} = \frac{V_1}{\gamma} \left[(\gamma - 1) \frac{P_2}{P_2} + \frac{P_1}{P_2} \right]$$

$$V_2 = \frac{V_1}{\gamma} \left[(\gamma - 1) + \frac{P_1}{P_2} \right]$$ Checar unidades

Tambien se puede obtener como Función de p2

$$p_2 v_2 = \frac{v_1}{\gamma}\left[(\gamma-1)\, p_2 + p_1\right]$$

$$p_2 v_2 = \frac{v_1}{\gamma}(\gamma-1)\, p_2 + \frac{v_1 p_1}{\gamma}$$

$$p_2 v_2 - \frac{v_1}{\gamma}(\gamma-1)\, p_2 = \frac{v_1 p_1}{\gamma}$$

$$p_2\left[v_2 - \frac{v_1}{\gamma}(\gamma-1)\right] = \frac{v_1 p_1}{\gamma}$$

$$p_2 = \left\{ \frac{\frac{V_1 P_1}{\gamma}}{\left[V_2 - \frac{V_1}{\gamma}(\gamma - 1) \right]} \right\}$$

Ejercicio obtener la relación T vs V

y terminar la comparación de exp. Adiab Rev. y exp. Adib. Irrev.

Con los datos del problema anterior

$T_1 = 300\,K$ $p_1 = 1.5\,atm$ $n = 3\,mol\ H_2$ $V_1 = 49.2\,L$

A partir de

$$T_2 = \frac{T_1}{\gamma}\left[(\gamma-1)\frac{P_2}{P_1}+1\right]$$ Sustituyendo

$$T_2 = \frac{T_1}{\gamma}\left[(\gamma-1)\frac{\cancel{n}RT_2/v_2}{\cancel{n}RT_1/v_1}+1\right]$$ eliminando

$$\frac{T_2}{T_1}\gamma = \left[(\gamma-1)\,\frac{T_2/V_2}{T_1/V_1} + 1\right]$$

$$\frac{T_2}{T_1}\gamma = \left[(\gamma-1)\,\frac{T_2 V_1}{T_1 V_2} + 1\right]$$

$$\frac{T_2}{T_1}\gamma = (\gamma-1)\frac{T_2}{T_1}\,\frac{V_1}{V_2} + 1$$

$$\frac{T_2}{T_1}\gamma - (\gamma-1)\frac{T_2}{T_1}\,\frac{V_1}{V_2} = 1$$

$$\frac{T_2}{T_1}\left[\gamma - (\gamma-1)\frac{V_1}{V_2}\right] = 1$$

$$T_2 = \frac{T_1}{\left[\gamma - (\gamma-1)\frac{V_1}{V_2}\right]}$$

Resolviendo el problema anterior para comparar la Exp. Adiab. Rev. contra la Exp. Adiab. Irrev.

Resolución

Predicción — Exp. Adiabática

$Q=0$

Rev		Irrev.
P_2	$<$	P_2
T_2	$<$	T_2
V_2	$=$	V_2
ΔU	$>$	ΔU
ΔH	$>$	ΔH
ΔS	$<$	ΔS

Cálculo para proceso irreversible

$V_2 = 2V_1$

$$T_2 = \frac{T_1}{\left[\gamma - (\gamma - 1)\frac{V_1}{V_2}\right]} = \frac{300\,K}{\left[1.4 - (1.4-1)\,\frac{1}{2}\right]} = 250\,K$$

$$P_2 = \left[\frac{V_1 P_1/\gamma}{\left(V_2 - \frac{V_1}{\gamma}(\gamma - 1)\right)}\right] = \left[\frac{(49.24\,L)(1.5\,atm)/1.4}{\left(98.4\,L - \frac{49.24\,L}{1.4}(1.4-1)\right)}\right] = \frac{52.7142\,atm\,L}{89.34\,L}$$

$$= 0.6249\,atm$$

$$W_{irrev} = p_2(V_2 - V_1)$$

$$= 0.6249\ \text{atm}\,(98.4\,L - 49.2\,L) = 30.7450\ \text{atm}\,L$$

$$= (30.7450\ \text{atm}\,L)\left(\frac{1.01325\times10^5\ N/m^2}{\text{atm}}\right)\left(\frac{1\,m^3}{10^3\,L}\right) = 3117.6\ J$$

$$\Delta U = -W = -3117.6\ J$$

$$\Delta H = \frac{7}{5}\Delta U = \frac{7}{5}(-3117.6\ J) = -4551.915\ J$$

ΔS_{irrev} deducción

$$\Delta S_{irrev} = \frac{Q}{T} = \frac{\Delta U + W}{T}$$

$$\int_1^2 \delta S_{irrev} = \frac{dU + \delta W}{T} = \int_1^2 \frac{n\bar{C}_V\, dT + p\, dV}{T}$$

si $p = \frac{nRT}{V}$

$$\Delta S_{irrev} = n\bar{C}_V \int_{T_1}^{T_2} \frac{dT}{T} + nR \int_1^2 \frac{dV}{V}$$

$$\Delta S_{irrev} = n\left[\bar{C}_V \ln\frac{T_2}{T_1} + R\ln\frac{V_2}{V_1}\right]$$

Sustituyendo

$$\Delta S_{irrev} = 3\,mol \left[\frac{5}{2}(8.314\ J/molK) \ln \frac{250K}{300K} + \frac{8.314\ J}{molK} \ln \frac{98.4L}{49.2L} \right]$$

$$= 3\,mol \left[-3.7895 \frac{J}{molK} + 5.76 \frac{J}{molK} \right]$$

$$= 5.9\ J/K$$

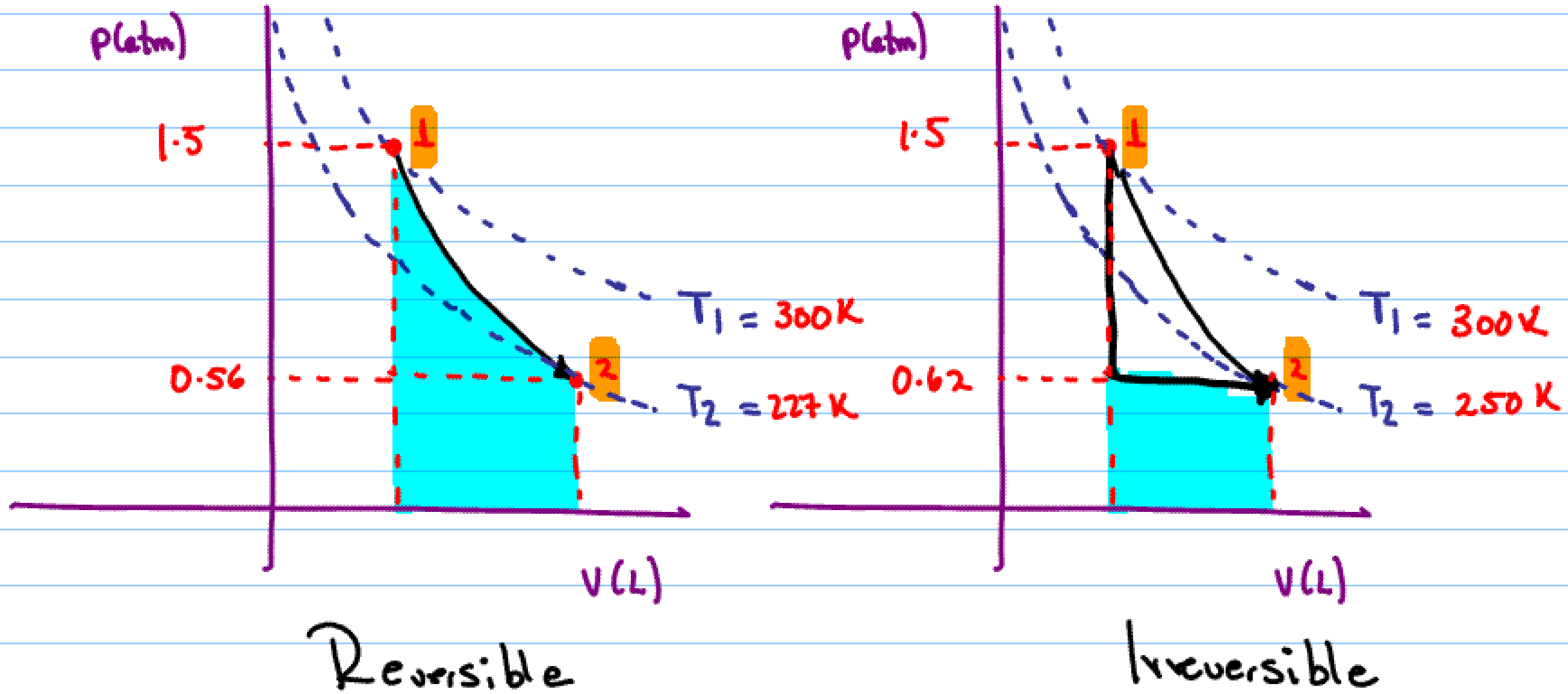
Se cumple segunda Ley Termodinámica

Aumento de entropía en proceso irreversible

Tabla comparativa Expansión Adiabática

Rev.		Irrev.
98.4	V_2 (L)	98.4
0.5683	P_2 (atm)	0.6249
227.53	T_2 (K)	250
−4551.9	ΔU (J)	−3117.7
−6372.7	ΔH (J)	−4364.85
0	Q (J)	0
0	ΔS (J/K)	5.9 J/K

Diagrama p vs V Exp. Adiabatica



Conclusiones (Expansión Adiabática)

$W_R > W_{irrev}$ $W = +$ expansión genera más trabajo el proceso reversible ✓

✓ $T_{2_{Rev}} < T_{2_{irrev}}$ el sistema se enfría más en forma reversible

✓ $P_{2_{Rev}} < P_{2_{irrev}}$

✓ $\Delta H_R > \Delta H_{irrev}$

✓ $\Delta S_{irrev} > \Delta S_{Rev}$

es favorable el proceso irreversible de expansión

Mayor reducción de energía interna en el proceso reversible

✓ $\Delta U_R > \Delta U_{irrev}$