VIII: TERMOQUÍMICA

> Propiedades intensivas y extensivas

- Vol. específico: $v = \frac{V}{m} \left[\frac{m^3}{kg}\right]$
- Vol. molar: $VM = \frac{V}{n} \left[\frac{m^3}{mol}\right]$
- densidad: $\rho = \frac{1}{v} \left[\frac{kg}{m^3}\right]$
- Gases ideales: $PV = nRT$

* $R = 0{,}082 \frac{atm \cdot L}{mol \cdot K}$

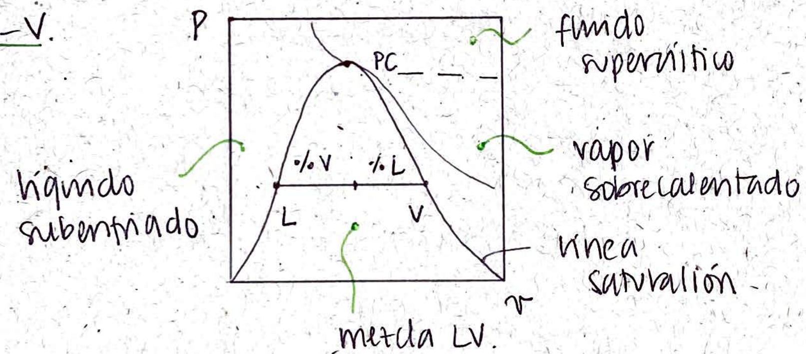
* SISTEMAS

- Abierto: vol fijo (E y mat ↑↓)
- Cerrado: no flujo materia, sí energía.
- Aislado: NADA.
- Adiabático: no intercambia calor.

$P = F/A$ (Pa, bar, atm).

> Diagramas

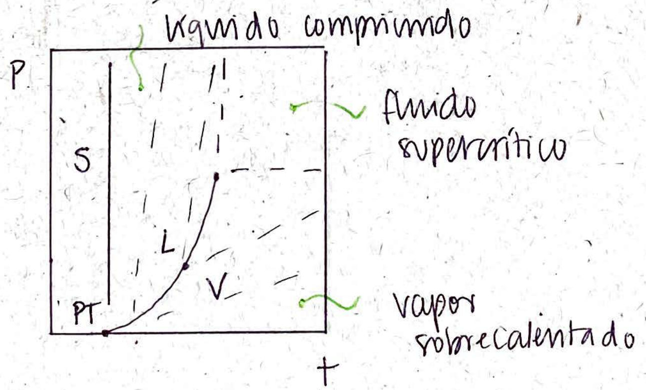
- P–V.



VSC: $P < P_{sat}$, $T > T_{sat}$

LSE: $P > P_{sat}$, $T < T_{sat}$.

- P–T.



– – – vol. cte.

- Calidad: $x^v = \frac{v_D - v_L}{v_v - v_L}$ $\Rightarrow v = v_L + x^v (v_g - v_L)$

(campana)

Fracción másica.

> Trabajo

$W = -\int P_{ext}\, dV$: Sale del sist. $V_f > V_i$

$W = \int P_{ext}\, dV$: Sobre el sist. $V_f < V_i$

$J = Pa \cdot m^3$

> 1RA LEY

$(J/s = Watts)$

$W = \int P dV$

$\Delta E = Q + W$

$\Delta E = \underset{cin}{\Delta E_K} + \underset{pot}{\Delta E_P} + \underset{int.}{\Delta U} = \Delta W_{AB}$

adiab: $\Delta E = \Delta U$.

- Vol constantes : $Q = \Delta U$
- Presión constante : $Q = \Delta H$.

* $h = h_L + x^v (h_g - h_L)$

$u = u_L + x^v (u_g - u_L)$

irrev. : no nota p.int

rev : cómo cambia p.int

$W_{rev} = -nRT \cdot \ln\left(\frac{V_f}{V_i}\right)$

> Calor

- Capacidad calorífica: $C = \frac{\delta Q}{\delta t}$ "calor específico"

* V. cte : $C_v = \left(\frac{\delta U}{\delta t}\right)_V$

* P cte : $C_p = \left(\frac{\delta H}{\delta t}\right)_P$

$Q = \Delta H = mC_p \Delta T$ (sensible)

* Interpolación:

T	v
a	b
x	c
d	e

$(y - y_0) = (x - x_0)m$.

$c = \frac{e-b}{d-a}(x-a) + b$

$y = y_0 + \frac{(y_2 - y_0)}{(x_2 - x_0)}(x - x_0)$

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→ Gases ideales

$PV = nRT$ $\qquad PV_m = RT$ $\qquad Pv = \frac{RT}{Mw}$

$+T^{\circ}\ +V.$

$C_p - C_v = R$

$\Delta u = \int C_v \cdot dT$ $\qquad \gamma = \frac{C_p}{C_v}$

$\Delta h = \int C_p \cdot dT$

- Isotérmico. $(\gamma = 1)$

$\Delta U = \Delta H = Q + W = 0.$

$Q = nRT \ln\left(\frac{P_1}{P_2}\right)$

- Isocórico $(\gamma = 0)$

$Q = \Delta U \quad (W=0) = \int n\,C_v\,dT$ $\qquad * \ \Delta H = \int n\,C_p\,dT.$

$\left(\frac{P_1}{P_2}\right) = \left(\frac{T_1}{T_2}\right)$

- Isobárico $(\gamma = \infty)$

$Q = \Delta H = \int n\,C_p\,dT \qquad W = -P\int dV.$

- Adiabático ( )

$Q = 0 \qquad \Delta U = W = \int n\,C_v\,dT$ $\qquad PV^{\gamma} = cte$

$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{\gamma-1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$

- Poliprótico. isoentrópico

$\Delta U = Q + W \qquad W = \left(\frac{R}{1-k}\right)\Delta T \cdot n$ $\qquad Pv^{k} = cte.$

$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{k-1} = \left(\frac{P_2}{P_1}\right)^{\frac{k-1}{k}}$

→ Gases reales

$Z = \frac{PV}{nRT}$

- Lee Kesler: $\quad Z = Z^{(0)} + w Z^{(1)}$

- Tsnopolus: $\quad \frac{BP_c}{RT_c} = B^{(0)} + wB^{(1)}$ $\qquad * \ P_r = \frac{P}{P_c} \qquad T_r = \frac{T}{T_c}$

- Van der Waals

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \qquad a = \frac{27}{64} \cdot \frac{(RT_c)^2}{P_c}$$

$$b = RT_c / 8P_c.$$

- SRK ^ Peng-Robinson.

→ Entropía 2DA LEY: entropía total universo debe incrementar.

Dirección y espontaneidad; aumenta hasta equilibrio.

- Abierto:

$$\frac{dS}{dt} = \frac{\dot{Q}}{T} + \sum \dot{m}_i \cdot s_i + \dot{S}_{gen}$$

+ 0 − s_i + 0 − Q.

T → fuente.

- Cerrado: $\sum \dot{m}_i \cdot s_i = 0$

rev: $\dot{S}_{gen} = 0$

$$ds = \int \frac{dQ}{T} = c_p \ln\left(\frac{T_2}{T_1}\right) - R\ln\left(\frac{P_2}{P_1}\right)$$

- Adiabático: $Q_{rev} = 0$

$$\int \frac{C \cdot m \cdot dT}{T}$$

- CR, P cte $\quad ds = C_p \cdot \ln\left(\frac{T_2}{T_1}\right)$

CR, V cte $\quad ds = C_v \ln\left(\frac{T_2}{T_1}\right)$

CR, T cte $\quad ds = c_p \ln\left(\frac{T_2}{T_1}\right) - R\ln\left(\frac{P_2}{P_1}\right)$

$$+ R\left(\frac{V_2}{V_1}\right)$$

- Vaporización: $\Delta S = s_g - s_l = \frac{\Delta H_{vap}}{T_{sat}}$

$$s = s_l + x(s_g - s_l)$$

→ Máquinas térmicas

- Da Q a W en ciclos.

* Clausius: no hay MT que único obj sea Q de fría a caliente. debo agregar W.

* Kevin-Plack: no hay MT que único obj sea Q → W.

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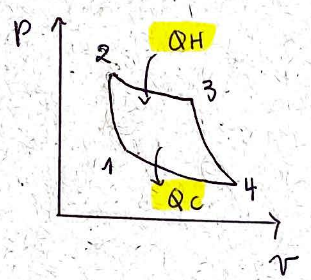
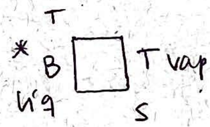
Ciclo de Carnot



(1-2): comp. adiabática
(2-3): exp. isotérmica
(3-4): exp. adiabática
(4-1): comp. isotérmica.

$\eta = 1 - \frac{T_C}{T_H}$

tasa rechazo mín.: $\frac{Q_L}{W} = \frac{1-\eta}{\eta}$



$W = Q_{in} - Q_{out}$

$\eta = \frac{W}{Q_{in}\,(H)} = 1 - \frac{Q_{out}}{Q_{in}}$

MOTOR COMBUSTIÓN EXTERNA

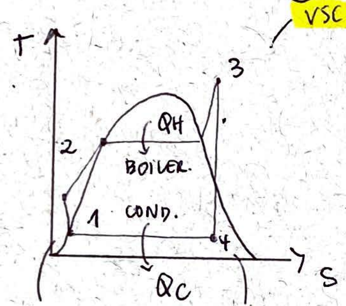
* Rankine:

$Q_H = h_3 - h_2$

$w_T = h_3 - h_4$

$Q_C = h_1 - h_4$

$w_B = h_1 - h_2$.

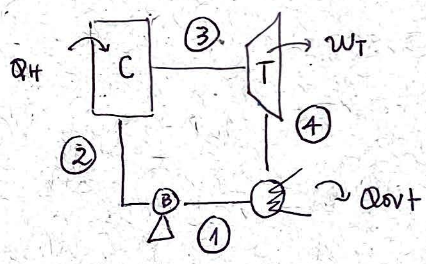


(i) VSC: $P_2 = P_3$.

(1-2): bombeo.
(2-3).
(3-4): exp. isoentrópica
(4-1): con líq sat.

$\eta = \frac{(h_3 - h_4) - (h_2 - h_1)}{h_3 - h_2}$.

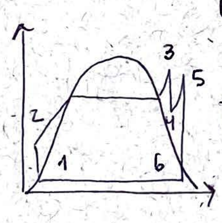
$BWR = \frac{w_B}{w_t}$.



(ii) turbina: $s_1 = s_2$ $v_1 = v_2$

(iii) bomba: $(h_2 - h_1) = v_2 (P_2 - P_1)$.

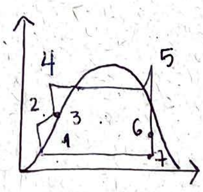
Recalentamiento



(2Turb)
3-4 ⊖
5 →
} VSC. $(s_5 = s_6)$ (i)

$W_{neto}: (h_1 - h_2) + (h_3 - h_4) - (h_6 - h_5)$

Regeneración

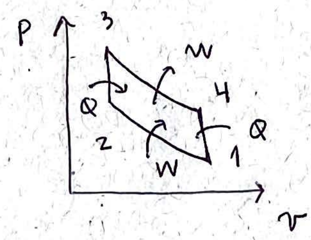


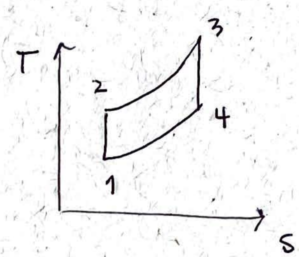
(i) → VSC $(s_5 = s_6 = s_7)$
(ii) 6, 7: L-V $(s \to h)$
(iii) 1: líq. sat.
$h_1 = h_f$
$v_1 = v_f$.
(iv) 2: líq subenf.
$w_{B1} = (h_2 - h_1) = v_1 (P_2 - P_1)$.
3: líq sat
(v) líq. subenf.

- MOTR COMBUSTIÓN INTERNA

Bujía prende chispa y entra aire + comb. por válvula.

* Otto:





(1-2): comp. isoentrop

(2-3): +Q a Vcte

(3-4): exp. isoentrop.

(4-1): −Q a Vcte.

$w_{12} = u_2 - u_1$

$Q_{23} = u_3 - u_2$

$|w_{34}| = u_4 - u_3$

$Q_{41} = u_1 - u_4$

$w_{neto} = (u_3 - u_4) - (u_2 - u_1)$

$$\eta = \frac{W_n}{Q_{in}}$$

- TABLA ESTÁNDAR AIRE

$v_{r2} = \frac{v_{r1}}{r}$, $v_{r4} = v_{r3} \cdot r$

$$r = \frac{v_1}{v_2} = \frac{v_4}{v_3}$$

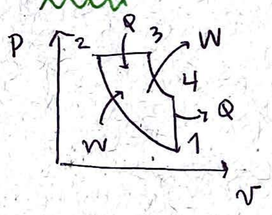
- aire frío: $\eta = 1 - \frac{T_1}{T_2} = 1 - \frac{1}{r^{k-1}}$

$T_2 = T_1 \cdot r^{k-1}$

$T_4 = T_3 / r^{k-1}$

$P_2 = P_1 \cdot \frac{T_2 \cdot r}{T_1}$ (Vcte) GAS IDEAL.

* Diesel

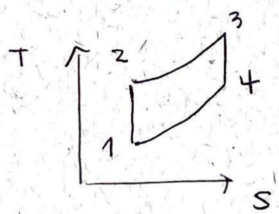


(1-2): comp. isoentrópica

(2-3): +Q a Pcte

(3-4): exp. isoentrópica

(4-1): −Q a Vcte



$r_c = \frac{v_3}{v_2}$ $r = \frac{v_1}{v_2}$

$w_{12} = u_2 - u_1$

$Q_{23} = h_3 - h_2$

$|w_{34}| = u_4 - u_3$

$|Q_{41}| = u_4 - u_1$

$T_3 = r_c T_2$

$$\frac{T_4}{T_3} = \left(\frac{r_c}{r}\right)^{k-1}$$

$$\eta = 1 - \frac{1}{r^{k-1}} \frac{[r^k - 1]}{[k(r-1)]}$$

$v_{r4} = \frac{r}{r_c} v_{r3}$

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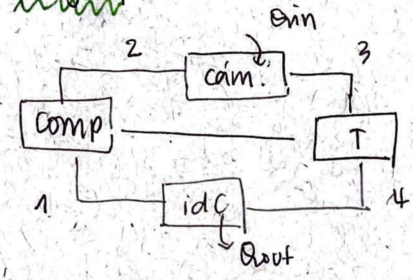
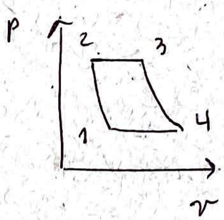
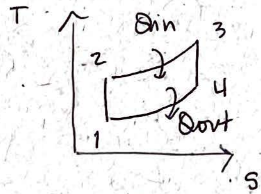
* Brayton







$$w_c = h_2 - h_1$$
$$|w_T| = h_3 - h_4$$
$$Q_{in} = h_3 - h_2$$
$$|Q_{out}| = h_4 - h_1$$

$$\eta = \frac{(h_3 - h_4) - (h_2 - h_1)}{(h_3 - h_2)}$$

$$BWR = \frac{h_2 - h_1}{h_3 - h_4}$$

Base estandar

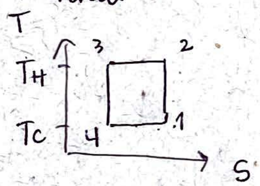
$$r_p = P_2 / P_1$$
$$Pr_2 = \frac{P_2}{P_1} \cdot Pr_1$$
$$Pr_4 = \frac{P_4}{P_3} \cdot Pr_3$$

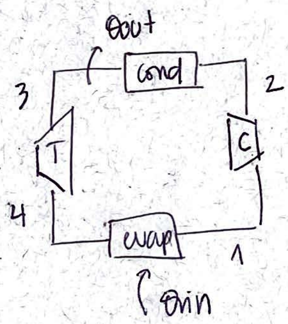
Base aire frío.

$$T_2 = T_1 \left(\frac{P_2}{P_1}\right)^{k-1/k}$$
$$T_4 = T_3 \cdot \left(\frac{P_4}{P_3}\right)^{\frac{k-1}{k}}$$
$$\eta = 1 - T_1/T_2 = 1 - \frac{1}{r_p^{(k-1)/k}}$$

* Refrigeración

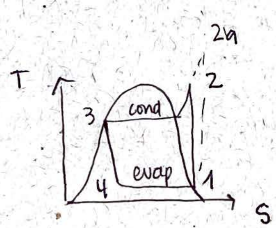
ideal





$$COP = \frac{T_C}{T_H - T_C}$$

c = L



$$\eta_c = \frac{h_{2s} - h_1}{h_2 - h_1}$$

$$w_c = h_2 - h_1$$
$$|Q_o| = h_2 - h_3 \qquad h_3 = h_4$$
$$Q_{in} = h_1 - h_4$$

$$COP_R = \frac{Q_{in}}{w} = \frac{h_1 - h_4}{h_2 - h_1}$$