

# Clase 23 8 Septiembre 2014

Título de la nota

08/09/2014

gases perfectos  $\left\{ \begin{array}{l} \bar{C}_p \\ \bar{C}_v \end{array} \right\}$  ctes

gases ideales  $\left\{ \begin{array}{l} \bar{C}_p \\ \bar{C}_v \end{array} \right\} f(T) = a + bT + cT^2 + dT^3$   
cal/molK ó J/molK  
 $a, b, c, d = \text{ctes para cada gas}$

Si se aplica al cálculo de  $\Delta U$  y  $\Delta H$

$$dH = n\bar{c}_p dT \quad dU = n\bar{c}_v dT$$

$$dH = n \left[ a + bT + cT^2 + dT^3 \right] dT$$

$$\int_1^2 dH = n \left[ \int_{T_1}^{T_2} (a + bT + cT^2 + dT^3) \right] dT$$

Separando

$$\Delta H = n \left[ a \int_{T_1}^{T_2} dT + b \int_{T_1}^{T_2} T dT + c \int_{T_1}^{T_2} T^2 dT + d \int_{T_1}^{T_2} T^3 dT \right]$$

$$\Delta H = n \left[ a (T_2 - T_1) + \frac{b}{2} (T_2^2 - T_1^2) + \frac{c}{3} (T_2^3 - T_1^3) + \frac{d}{4} (T_2^4 - T_1^4) \right]$$

Agregando unidades

$$\text{Si } \bar{C}_p f(T) = \text{cal/molK}$$

$$\Delta H = \cancel{\text{mol}} \left[ a \frac{\cancel{\text{cal}}}{\cancel{\text{molK}}} (\cancel{K} - \cancel{K}) + \frac{b}{2} \frac{\cancel{\text{cal}}}{\cancel{\text{molK}^2}} (\cancel{K}^2 - \cancel{K}^2) + \frac{c}{3} \frac{\cancel{\text{cal}}}{\cancel{\text{molK}^3}} (\cancel{K}^3 - \cancel{K}^3) \dots \right]$$

$\Delta H = \text{cal}$  de esta forma

$$a = \text{cal/molK}$$

$$b = \text{cal/molK}^2$$

$$c = \text{cal/molK}^3$$

$$d = \text{cal/molK}^4$$

unidades de cada constante

En el caso de  $\Delta U$

$$\bar{C}_V = (\bar{C}_P - R) \text{ aplicando}$$

$$dU = n \bar{C}_V dT$$

$$\bar{C}_P f(T) = a + bT + cT^2 + dT^3$$

$$\int_1^2 dU = n \int_{T_1}^{T_2} \left[ (a - R) + bT + cT^2 + dT^3 \right] dT$$

Importante

R mismas unidades que a

si  $a = \text{J/molK}$   $R = \text{J/molK}$   
si  $a = \text{cal/molK}$   $R = \text{cal/molK}$

Resolviendo

$$\Delta U = n \left[ (a-R) \int_{T_1}^{T_2} dT + b \int_{T_1}^{T_2} T dT + c \int_{T_1}^{T_2} T^2 dT + d \int_{T_1}^{T_2} T^3 dT \right]$$

$$\Delta U = n \left[ (a-R)(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) + \frac{c}{3}(T_2^3 - T_1^3) + \frac{d}{4}(T_2^4 - T_1^4) \right]$$

Unidades

$$\Delta U = \cancel{\text{mol}} \left[ \frac{\text{cal}}{\cancel{\text{mol}}\cancel{\text{K}}} - \frac{\text{cal}}{\cancel{\text{mol}}\cancel{\text{K}}} (\cancel{x} - \cancel{y}) + \frac{\text{cal}}{\cancel{\text{mol}}\cancel{\text{K}^2}} (\cancel{x}^2 - \cancel{y}^2) + \frac{\text{cal}}{\cancel{\text{mol}}\cancel{\text{K}^3}} (\cancel{x}^3 - \cancel{y}^3) + \frac{\text{cal}}{\cancel{\text{mol}}\cancel{\text{K}^4}} (\cancel{x}^4 - \cancel{y}^4) \right]$$

$$\Delta U = \text{cal}$$

Recordar gases

ideales y perfectos

$$\Delta U < \Delta H$$



Ejercicio Máquina refrigerante

(gas ideal  $O_2$ )

$$T_c = 400 \text{ K} \quad T_F = 300 \text{ K}$$

$$V_1 = ? \quad p_1 = 1 \text{ atm} \quad V_2 = \frac{1}{2} V_1$$

Dibujar el refrigerador de Carnot

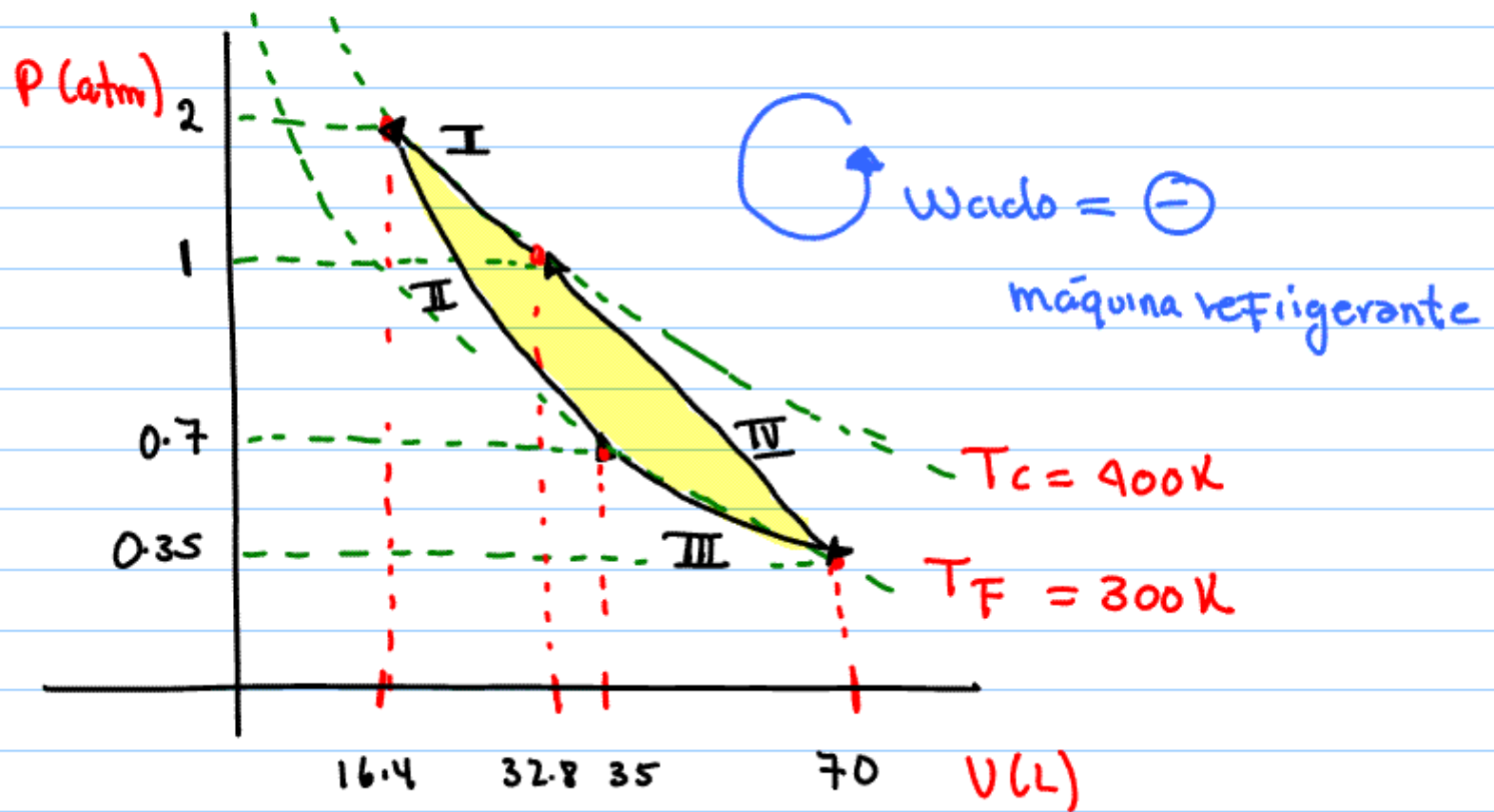
Calcular el Coeficiente de operación

$$\bar{C}_p f(T) \text{ Oxígeno} = 6.10 + 3.25 \times 10^{-3} T - 1.02 \times 10^{-6} T^2 \quad \text{cal/molK}$$

rango aplicación (300-2500)K



# El diagrama p vs V (Refrigerador) Tipo Carnot



## I Cálculo de variables

$$p_1 = 1 \text{ atm} \quad T_1 = 400 \text{ K} \quad n = 1 \text{ mol } O_2$$

$$V_1 = \frac{nRT_1}{p_1} = 32.8 \text{ L}$$

$$V_2 = \frac{1}{2} V_1 = 16.4 \text{ L}$$

$$p_2 = p_1 \left( \frac{V_1}{V_2} \right) = 1 \text{ atm} \left( \frac{V_1}{\frac{1}{2} V_1} \right) = 2 \text{ atm}$$

$$T_2 = T_1 \quad T_3 = T_2 \left( \frac{V_2}{V_3} \right)^{\gamma-1} \quad \left( \frac{T_3}{T_2} \right)^{\frac{1}{\gamma-1}} = \frac{V_2}{V_3}$$

$$V_3 = \frac{V_2}{\left( \frac{T_3}{T_2} \right)^{\frac{1}{\gamma-1}}}$$

Obtención de  $\gamma$

$$R = 1.9889 \text{ cal/molK}$$

$$\gamma = \frac{\bar{C}_p f(T)}{\bar{C}_v f(T)} = \frac{6.10 + 3.25 \times 10^{-3} T - 1.02 \times 10^{-6} T^2}{(6.10 - 1.9889) + 3.25 \times 10^{-3} T - 1.02 \times 10^{-6} T^2}$$

La  $T = 400$  donde comienza el proceso adiabático

$$\gamma = \frac{6.10 + 3.25 \times 10^{-3} (400) - 1.02 \times 10^{-6} (400)^2}{(6.10 - 1.9889) + 3.25 \times 10^{-3} (400) - 1.02 \times 10^{-6} (400)^2} = 1.3789$$

retomando el cálculo de variables

$$V_3 = \frac{V_2}{\left(\frac{T_3}{T_2}\right)^{\frac{1}{1.3789-1}}} = 35.04 \text{ L}$$

de la relación  $\frac{V_2}{V_1} = \frac{V_3}{V_4} \therefore V_4 = \frac{V_1 V_3}{V_2} = \frac{(32.8 \text{ L})(35.04 \text{ L})}{(16.4 \text{ L})}$   
 $= 70.08 \text{ L}$

$$P_3 = P_2 \left(\frac{V_2}{V_3}\right)^{\gamma} = 2 \text{ atm} \left(\frac{16.4 \text{ L}}{35.04 \text{ L}}\right)^{1.3789} = 0.70 \text{ atm}$$

$$P_4 = P_3 \left(\frac{V_3}{V_4}\right) = 0.7 \left(\frac{35.04 \text{ L}}{70.08 \text{ L}}\right) = 0.35 \text{ atm}$$

## Cuadro de Variables

	P (atm)	V (L)	T (K)
1	1.0	32.8	400
2	2.0	16.40	400
3	0.70	35.04	300
4	0.35	70.08	300

### III Cálculo de Funciones de estado

I Comp. Isot. Rev.

$$\Delta U = 0 \quad \Delta H = 0 \quad Q = W$$

$$T_1 = T_c = 400\text{K}$$

$$\Delta S = nRT_c \ln \frac{V_2}{V_1} = -1.37 \text{ cal/K}$$

$$Q = \Delta S (T_1) = -1.37 \text{ cal/K} (400\text{K}) \\ = -551 \text{ cal}$$

## II Exp. Adiab. Rev.

$$\Delta U = 1 \text{ mol} \left[ \frac{6.10 - 1.9874}{\cancel{\text{molK}}} (\cancel{\text{K}}) (300 - 400) + \frac{3.25 \times 10^{-3}}{\cancel{\text{molK}^2}} (\cancel{\text{K}^2}) (300^2 - 400^2) - \frac{1.02 \times 10^{-6}}{\cancel{\text{molK}^3}} (\cancel{\text{K}^3}) (300^3 - 400^3) \right]$$

$$= -512.28 \text{ cal}$$

$$\Delta H = 1 \text{ mol} \left[ \frac{6.10}{\cancel{\text{molK}}} (\cancel{\text{K}}) (300 - 400) + \frac{3.25 \times 10^{-3}}{\cancel{\text{molK}^2}} (\cancel{\text{K}^2}) (300^2 - 400^2) - \frac{1.02 \times 10^{-6}}{\cancel{\text{molK}^3}} (\cancel{\text{K}^3}) (300^3 - 400^3) \right]$$

$$= -711.17 \text{ cal}$$

$$W = -\Delta U$$

$$Q = 0$$

$$\Delta S = 0$$

$$W = 512.28 \text{ cal}$$

III Exp. Isot. Rev.

$$\Delta U = 0 \quad \Delta H = 0 \quad Q = W$$

$$\Delta S = nR \ln \frac{V_4}{V_3} = 1.37 \text{ cal/K}$$

$$Q = \Delta S (T_3)$$

$$T_3 = T_F = 300 \text{ K}$$

$$Q = \left( 1.37 \frac{\text{cal}}{\text{K}} \right) (300 \text{ K}) = 413 \text{ cal}$$

$$W = Q = 413 \text{ cal}$$



#### IV Comp. Adiab. Rev.

$\Delta U$  lo mismo que en proceso II pero de signo contrario

$$\Delta U = 512.28 \text{ J}$$

$\Delta H$  mismo caso que en proceso II pero de signo contrario

$$\Delta H = 711.17 \text{ J}$$

$$\Delta S = 0 \quad Q = 0 \quad W = -\Delta U = -512.28 \text{ J}$$

## Cuadro de Funciones

	(cal) $\Delta U$	(cal) $\Delta H$	(cal/k) $\Delta S$	(cal) Q	(cal) W
I	0	0	-1.37	-551	-551
II	-512.28	-711.17	0	0	512.28
III	0	0	1.37	413	413
IV	512.28	711.17	0	0	-512.28
total	0	0	0	-138	-138

Coefficiente de operación o de ejecución

$$\text{COP} = \frac{T_F}{T_C - T_F} = \frac{300\text{K}}{400\text{K} - 300\text{K}} = 3$$

$$\text{COP} = - \frac{Q_F}{W_{\text{ciclo}}} = - \frac{Q_F}{Q_C - Q_F} = - \frac{Q_F}{W_{\text{ciclo}}}$$

para evitar ambigüedades de signos

$$\text{COP} = - \left[ \frac{413\text{ cal}}{-138\text{ cal}} \right] = 3$$

## Conclusiones

Ciclo con  $Q(-)$  exotérmico ✓

Funciones de estado  $\Delta U_c, \Delta H_c, \Delta S_c = 0$

Ciclo en equilibrio ✓

Trabajo del ciclo  $\ominus$   $W_{\text{ciclo}} \ominus$  se necesita aplicar trabajo para su funcionamiento ✓

Fte caliente  $T_c = 400\text{K}$

$\uparrow -551\text{cal}$

Refrigerador

$\leftarrow -138\text{J}$   
 $W_{\text{ciclo}}$

$\uparrow 413\text{cal}$

Fte Fría  $T_F = 300\text{K}$