FISICOQUIMICA

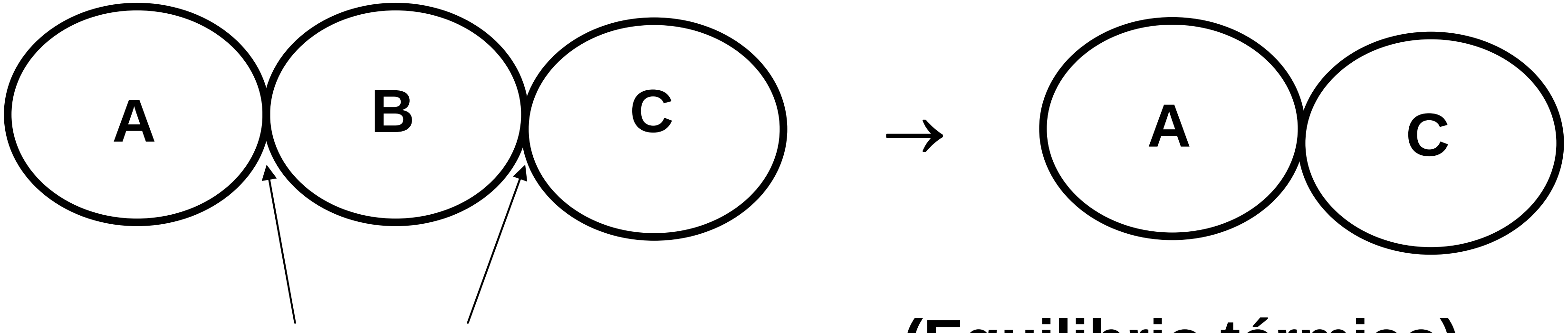
II.- TERMODINÁMICA

Sistema

P, T, V, Composición

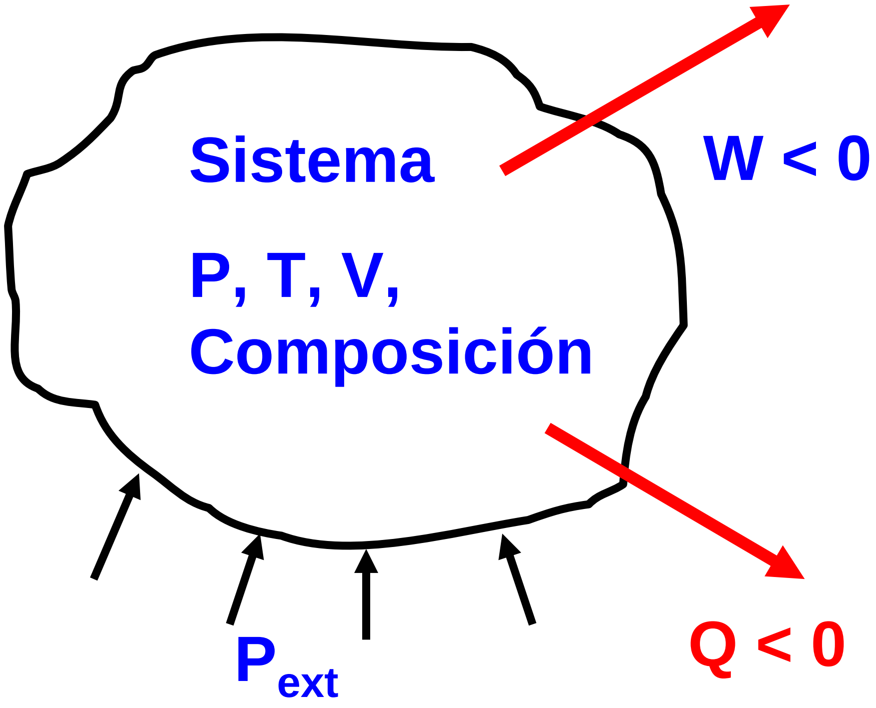
- **Abierto**
- **Cerrado**
- **Aislado**
- **Adiabático**
- **Estado**
- **Trayectoria**
- **Ciclo**

Ley Cero:



Contacto térmico

(Equilibrio térmico)



Sistema

P, T, V, Composición

$W < 0$

$Q < 0$

P_{ext}

$$W = -\int P_{ext}\, dV$$

Primera Ley:

$$\oint \left(d'Q + d'W \right) = \oint dE = 0 \qquad \forall\ Ciclo$$

$d'Q, d'W$ *Son diferenciales inexactas*

Cambios de Estado

$$(T_i, V_i, P_i) \rightarrow (T_f, V_f, P_f)$$ **Prop. Medibles**

$$E = E(T, V)$$

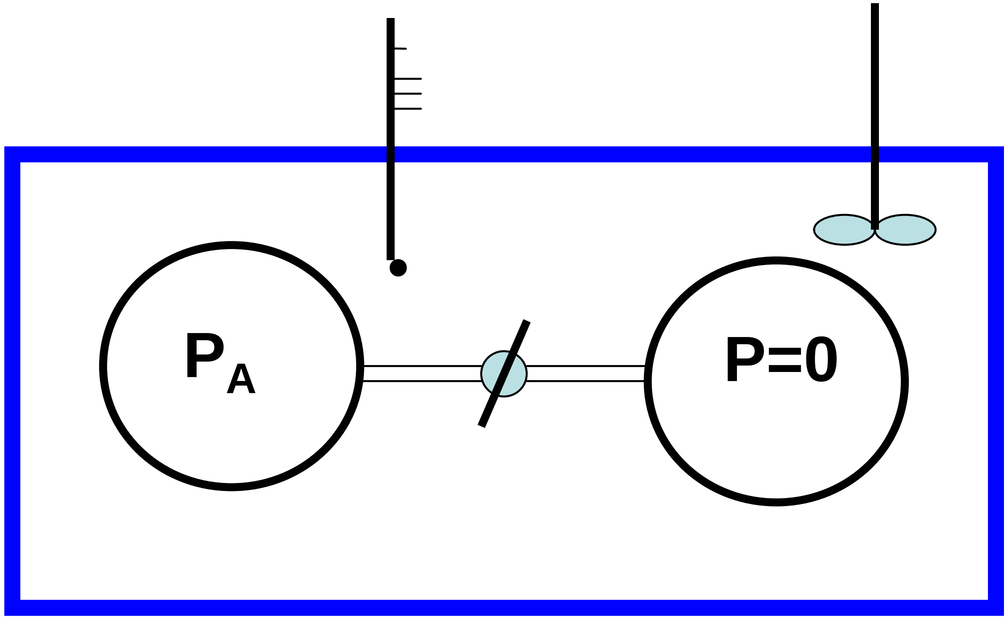
$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV = d'Q - P_{ext}dV$$

1) Cambio a V=Cte.

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT = C_V dT = d'Q_V$$

$$C_V = \left(\frac{\partial Q_V}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V \rightarrow \quad \Delta E = \int_{T_1}^{T_2} C_V dT = Q_V$$

Experimento de Joule

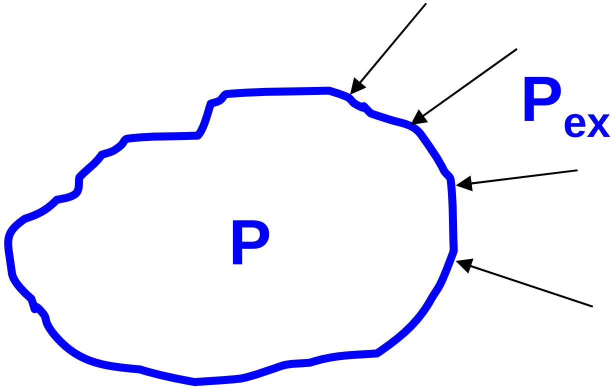


$$d'W = 0$$

$$dE = \left(\frac{\partial E}{\partial V}\right)_T dV = 0$$

Ley de Joule E= E(T)

2) Cambio a P = Cte.



$P = P_{ext} =$ Cte.

$$Q_P = (E_2 + P_2V_2) - (E_1 + P_1V_1)$$
$$= H_2 - H_1$$

$$\Delta E = Q_P - P(V_2 - V_1)$$

Entalpía: $\boxed{\mathrm{H = E + PV}}$ **Función de Estado**

H = H(P,T) →

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

P = Cte. →

$$\left(\frac{d'Q_P}{dT}\right)_P = C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

$$dH = C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

Proceso a P = Cte.

$$\Delta \mathrm{H} = \int_{\mathrm{i}}^{\mathrm{f}} \mathrm{C_P dT}$$

Relación entre C_P y C_V

$$d'Q = dE - d'W = C_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV + P_{ext} dV$$

$$Si \quad P = P_{ext} = Cte.$$

$$(d'Q_P) = C_V(\partial T)_P + \left(\frac{\partial E}{\partial V}\right)_T (\partial V)_P + P(\partial V)_P$$

$$C_P - C_V = \left[P + \left(\frac{\partial E}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$$

$$\frac{C_P}{C_V} = \gamma \qquad C_P \approx C_V \begin{cases} \text{Solidos} \\ \text{Liquidos} \end{cases}$$

Gases Ideales

$$C_P - C_V = \left[P + \left(\frac{\partial E}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_P = P \frac{\partial}{\partial T} \left(\frac{RT}{P} \right) = R$$

$$\frac{C_P}{C_V} = \gamma$$

Recordar: $$dH = C_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP \qquad \left(\frac{\partial H}{\partial P} \right)_T = ?$$

$$\rightarrow \quad C_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP = C_V dT + \left[P + \left(\frac{\partial E}{\partial V} \right)_T \right] dV + VdP$$

→ **Proceso isotermal**

→ Proceso isotermal

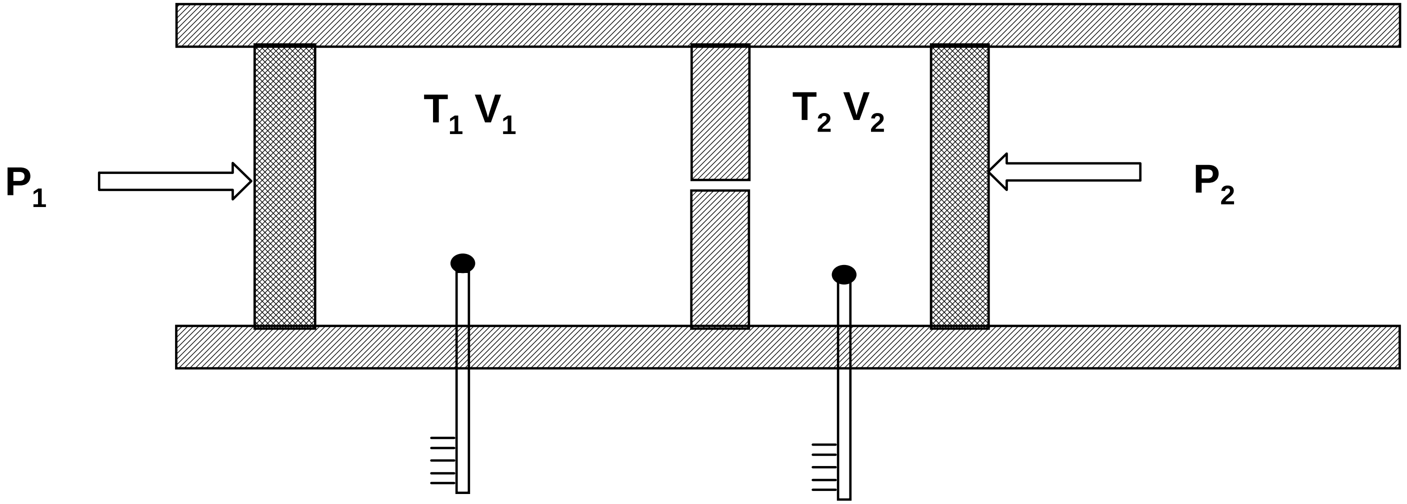
$$\left(\frac{\partial H}{\partial P}\right)_T = \left[\left(\frac{\partial E}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial P}\right)_T + V = ?$$

i) Sólido+líquidos: $\left(\frac{\partial V}{\partial P}\right)_T \approx 0$ $\left(\frac{\partial \overline{H}}{\partial P}\right)_T = \overline{V}$ **pequeño**

ii) Gas Ideal: $\overline{H} = \overline{E} + P\overline{V}$ $\left(\frac{\partial \overline{H}}{\partial P}\right)_T = 0$

iii) Gas Real: Experimento de Joule-Thomson

Experimento de Joule-Thomson



$$Q = 0; \qquad W_{neto} = P_1\overline{V}_1 - P_2\overline{V}_2 = \overline{E}_2 - \overline{E}_1$$

Proceso Isentálpico $dH = 0$

Medir $\left(\frac{\Delta T}{\Delta P}\right)_H$

Coeficiente de Joule-Thomson

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H$$

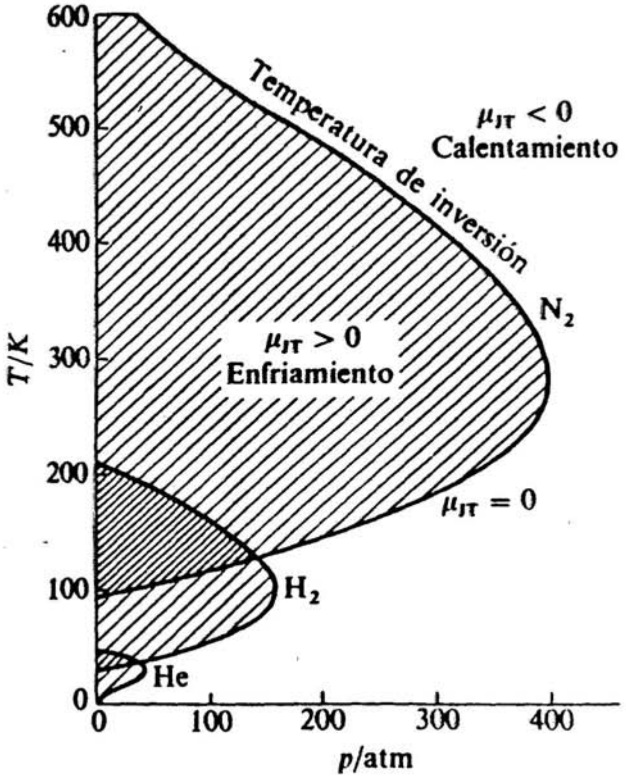
$$dH = 0 \quad \Rightarrow$$

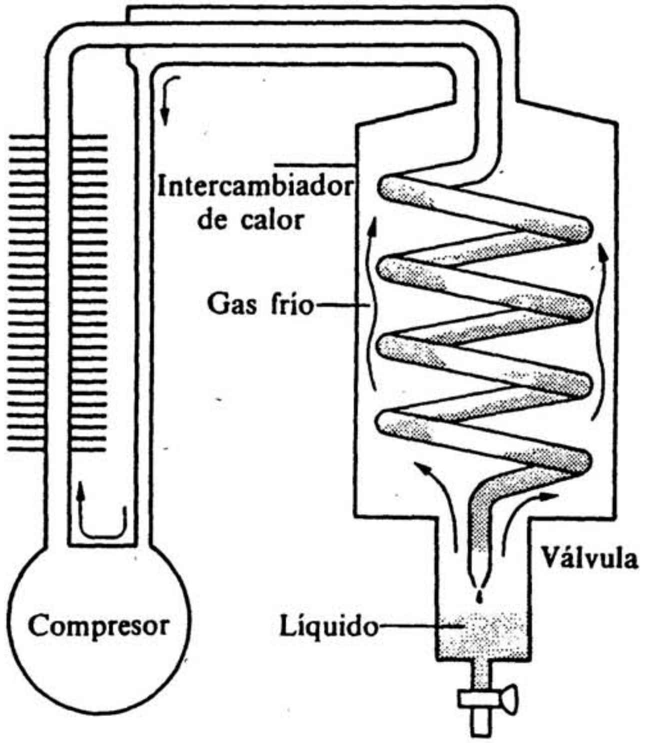
$$0 = C_P (\partial T)_H + \left(\frac{\partial H}{\partial P}\right)(\partial P)_H \qquad \therefore \boxed{\left(\frac{\partial H}{\partial P}\right) = -C_P\, \mu_{JT}}$$

Permite calcular:

$$\left(\frac{\partial H}{\partial P}\right)_T = -\overline{C}_P \mu_{JT} = \left[\left(\frac{\partial \overline{E}}{\partial \overline{V}}\right)_T + P\right]\left(\frac{\partial \overline{V}}{\partial P}\right)_T + \overline{V}$$

$$\uparrow$$


600
500
400
300
200
100
0
T/K
Temperatura de inversión
$\mu_{JT} < 0$
Calentamiento
N_2
$\mu_{JT} > 0$
Enfriamiento
$\mu_{JT} = 0$
H_2
He
0
100
200
300
400
p/atm


Intercambiador de calor
Gas frío
Compresor
Válvula
Líquido

$$\partial P < 0$$

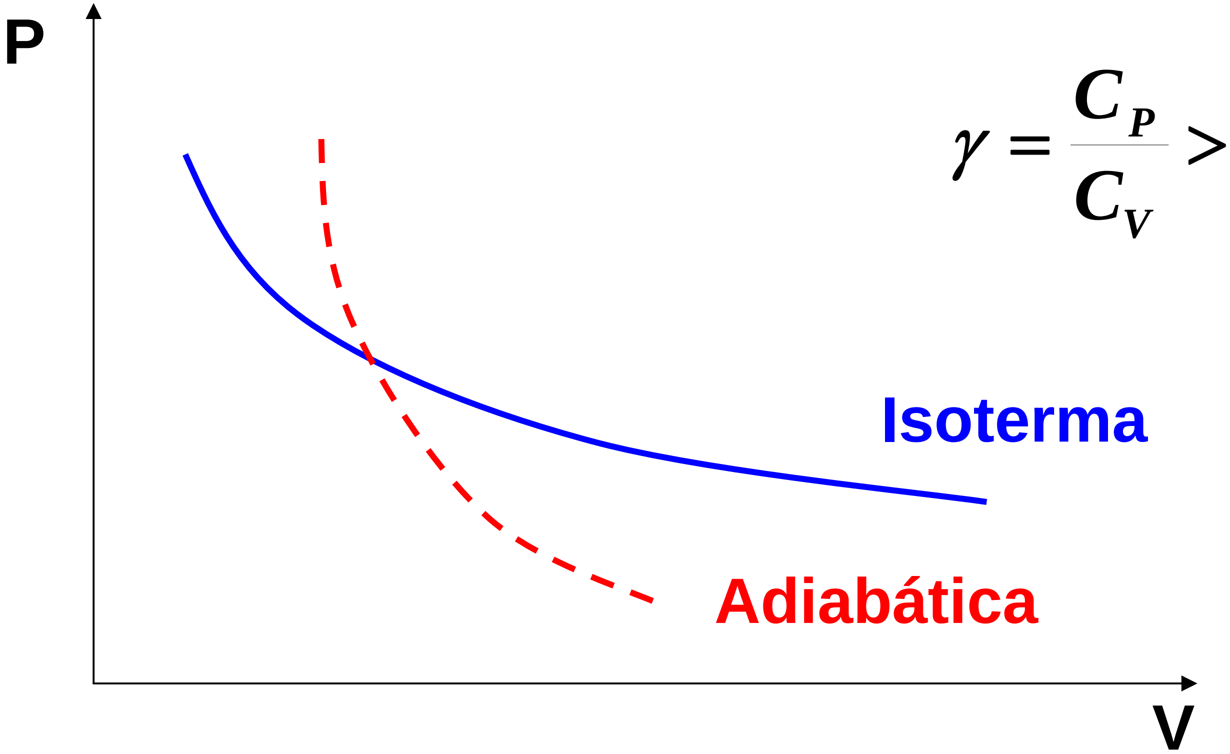
Procesos Adiabáticos $d'Q = 0 \quad \Rightarrow \quad dE = d'W$

Proceso Reversible (Gas Ideal)

$$\boxed{TV^{\gamma-1} = Cte}$$

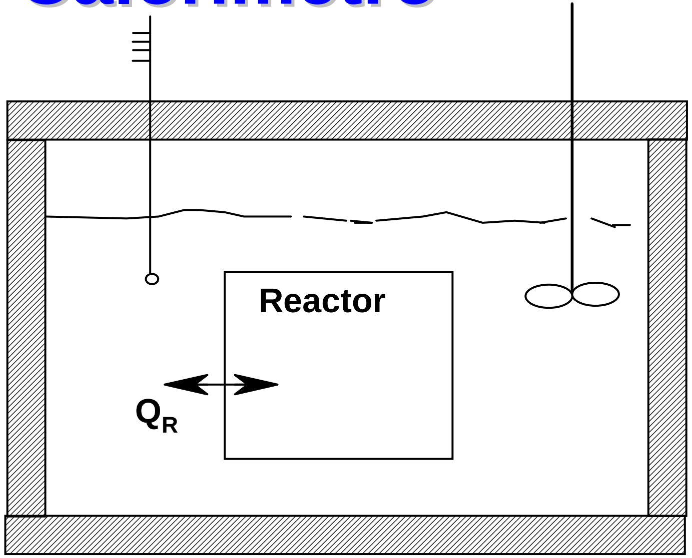
$$\boxed{PV^{\gamma} = Cte}$$

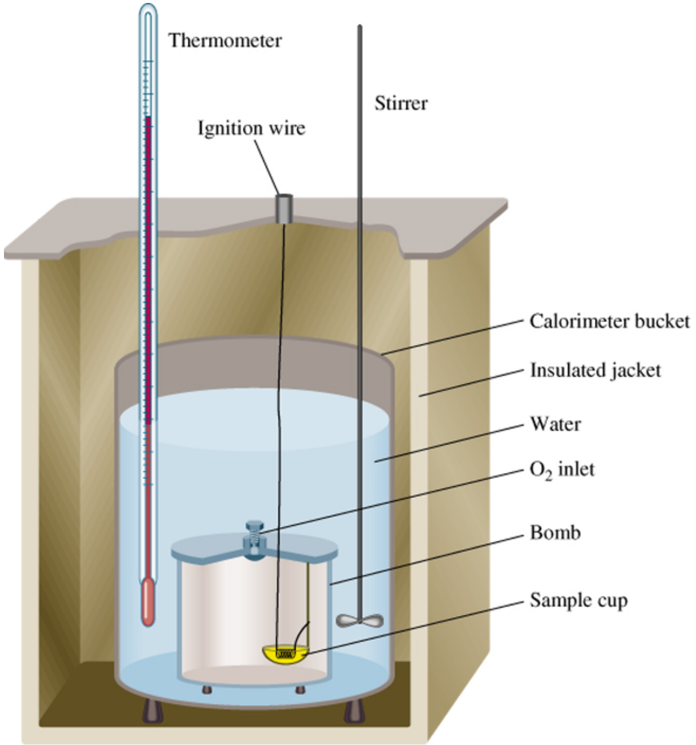
$$\boxed{T^{\gamma}P^{1-\gamma} = Cte}$$



$$\gamma = \frac{C_P}{C_V} > 1\left(\approx 1.4\right)$$

Calorímetro





$\mathbf{M}_{H_2O}$ = **Masa de agua**

$\mathbf{m}_C$ = **Equivalente en agua del Calorímetro**

- **Ecuación del Calorímetro**

$$0 = Q_R + \left(M_{H_2O} + m_C\right) C \left(T_f - T_1\right)$$

- **Equivalente en agua**

$$C_P \approx C_V$$

$$C = 1.0\left[\frac{\text{cal}}{°\text{C gr}}\right]$$

Calor Específico

Valores Estándar - Termoquímica

$$H = H(T,P)$$

$$\overline{H}^0 = H(T, P = 1\,atm) \quad \left[molar\right]$$

Entalpía a otra temperatura (P = Cte)

$$\overline{H}^0(T) = \overline{H}^0(T_0) + \int_{T_0}^{T} C_P^0(T)\,dT$$

En general:

$$C_P^0(T) = a + bT + cT^2 + dT^2 + \ldots$$

Entalpía de Reacción

$$a\,A + b\,B \longrightarrow c\,C + d\,D$$

(T,P) (T,P)

$$\Delta H^0_{Rxn} = \sum_P \nu_P \overline{H}^0_P - \sum_R \nu_R \overline{H}^0_R$$

estándar

Entalpía de Formación

$$\begin{pmatrix}\text{Elementos en}\\ \text{Estado estable}\end{pmatrix} \rightarrow \text{1 Molécula}$$

(T, P) (T, P)

PROPIEDADES TERMODINÁMICAS DE DIVERSAS SUSTANCIAS A 298.15 K (continuación)[¥]

Fórmula	Nombre	M (g/mol)	ΔH°_f (kJ/mol)	ΔG°_f (kJ/mol)	S°_f (J/mol K)	$C_{p,m}^\circ$ (J/mol K)
Carbono (continuación)						
$C_2H_{2\,(g)}$	acetileno	26.03	226.73	209.20	200.83	43.93
$C_3H_{8\,(g)}$	n-propano	44.09	-103.85	-23.56	270.20	73.60
$C_3H_{6\,(g)}$	propileno	42.08	20.42	62.84	266.60	64.31
$C_3H_7OH_{(l)}$	2-propanol	60.09	-317.86	-180.29	180.58	150.88
$C_3H_7OH_{(l)}$	1-propanol	60.09	-304.01	-170.62	194.56	141.00
$C_4H_{10\,(g)}$	n-butano	58.12	-126.15	-17.15	310.12	97.45
$C_4H_9OH_{(l)}$	1-butanol	74.12	-327.11	-162.51	226.35	177.03
$C_4H_9OH_{(l)}$	2-butanol	74.12	-342.59	-177.03	225.10	198.74
$C_5H_{12\,(g)}$	n-pentano	72.15	-146.44	-8.37	348.95	120.21
$C_6H_{14\,(l)}$	n-hexano	86.17	-198.70	-3.80	296.06	189.12
$C_6H_{12\,(l)}$	ciclohexano	84.16	-157.70	26.70	203.89	156.48
$C_6H_{6\,(l)}$	benceno	78.12	48.99	124.35	173.26	136.10
$C_6H_{6\,(g)}$	benceno	78.12	82.93	129.72	269.31	81.67

“Entalpía $\overline{\mathrm{H}}^0_{298}$ de los elementos a 298°K y 1.0 atm en su estado de agregación estable (S,L,G) es cero”

Ej.: H_2 (g), O_2 (g), Br (l), Hg (l), C (grafito), S (rómbico), Fe (s), etc.

Determinación de Calores de Formación

1) Directamente

$$\mathrm{H_2(g) + \tfrac{1}{2}O_2(g) \;\rightarrow\; H_2O(g)} \qquad \Delta \mathrm{H}^0_{\mathrm{f}} = -63.31\left[\frac{\mathrm{Kcal}}{\mathrm{mol}}\right]$$

2) Indirectamente

$$\mathrm{C(graf) + 2H_2(g) \;\rightarrow\; CH_4(g)} \qquad \Delta \mathrm{H}^0_{\mathrm{f}} = ??$$

(no es posible de realizar)

(combustión de metano)

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + H_2O(l) \qquad \Delta H^0_{comb} = \text{medible}$$

Luego:

$$\Delta H^0_{comb} = \overline{H}^0_{CO_2} + 2\overline{H}^0_{H_2O} - \overline{H}^0_{CH_4}$$

$$\overline{H}^0_{CH_4} = -94.5 + 2(-63.31) - (-212.79) = -17.89 \left[\frac{Kcal}{mol}\right]$$

LEY DE HESS

$$\begin{tikzcd}
\text{Reactantes} \arrow[rr, bend left, "\Delta H_1"] \arrow[rr, bend right, "\Delta H_2"'] & & \text{Productos}
\end{tikzcd}$$

$$\boxed{\Delta H_1 = \Delta H_2}$$

Ej.:

$$\begin{tikzcd}
& \mathrm{CO(g)} + \tfrac{1}{2}\mathrm{O_2(g)} \arrow[dr, "\Delta H_2"] & \\
\mathrm{C(graf)} + \mathrm{O_2(g)} \arrow[ur, "\Delta H_1"] \arrow[rr, "\Delta H_3"] & & \mathrm{CO_2(g)}
\end{tikzcd}$$

$$\Delta H_3 = \Delta H_1 + \Delta H_2$$

Calor de Solución y de Dilución

$$A + nA_q \xrightarrow{\Delta H_S} A \cdot nAq$$

Ej.: (Solución)

$$HCl(g) + 10Aq \rightarrow HCl \cdot 10Aq \qquad \Delta H_S = -16.61\left(Kcal/mol\right)$$

$$HCl(g) + 15Aq \rightarrow HCl \cdot 15Aq \qquad \Delta H_S = -17.27\left(Kcal/mol\right)$$

(Dilución)

$$HCl \cdot 10Aq + 5Aq \rightarrow HCl \cdot 15Aq \qquad \Delta H_{Dil} = -0.66\left(Kcal/mol\right)$$

Dependencia de ΔH^o_{reac} con T

$$\frac{d\Delta H^0_{reac}}{dT} = \frac{d\Delta H^0(Prod)}{dT} - \frac{d\Delta H^0(React)}{dT} = \Delta C^0_P$$

$$\int_{T_0}^{T} d\Delta H^0_{reac} = \int_{T_0}^{T} d\Delta C^0_P dT$$

$$\Delta C^0_P = \sum_{Prod} n_{Prod} C^0_P(Prod) - \sum_{React} n_{React} C^0_P(React)$$

Ejemplo:

$$Fe_2O_3(s) + 3H_2 \rightarrow 2Fe(s) + 3H_2O(l)$$

	$Fe_2O_3(s)$	$Fe(s)$	$H_2O(l)$	$H_2(g)$	
$\overline{C}^0_P$	25.0	6.1	18.0	6.9	(cal/mol)

Temperatura de llama adiabática:

i) React (T_0, P) → Prod (T_0, P) $\qquad \Delta H_{T_0}$

ii) Prod (T_0, P) → Prod (T_F, P) $\qquad \Delta H_2 = \int_{T_0}^{T_F} C_P(Prod)dT$

$$\Delta H_{Tot} = \Delta H_{T_0} + \int_{T_0}^{T_F} C_P(Prod)dT = 0$$

Ejemplo:

$(8N_2) + CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) + (8N_2)$

	a	b	c
$CO_2(g)$	6.369	10.100	-34.05
H_2O (g)	7.219	2.373	2.67
N_2 (g)	6.449	1.412	-0.87

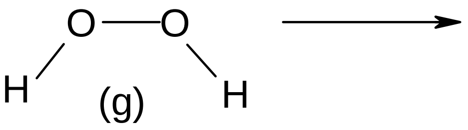
ΔH (Kcal/mol)	T_F
CH_4 = -17.9	~ 9188ºK
CO_2 = -94.0	~ 2622ºK
H_2O = -57.8	(en aire)

Energías de Enlace

i) Calor de atomización:

$$O_2(g) \rightarrow 2O(g) \qquad \Delta H^{0}_{298} = 118.318\ (Kcal/mol)$$

ii) Energía de enlace:

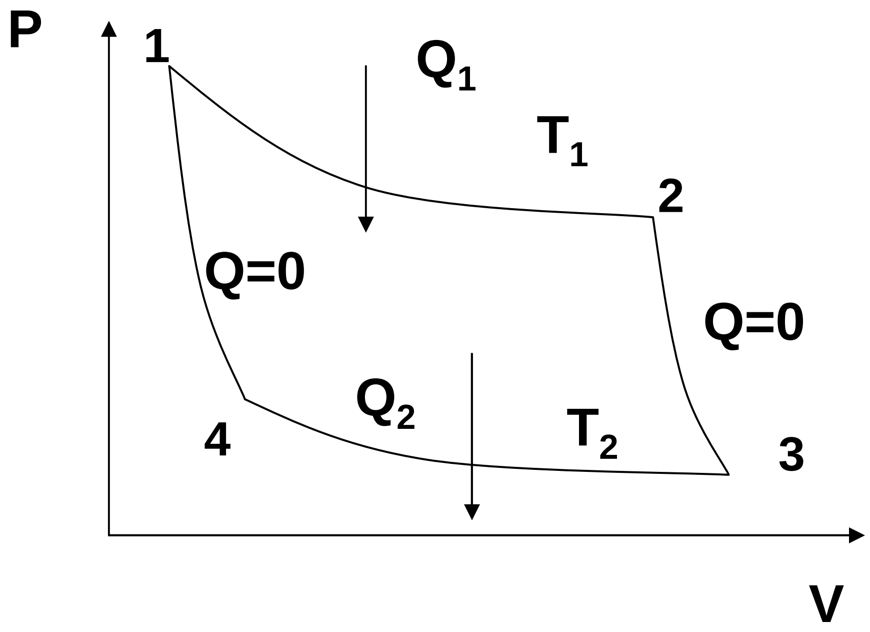


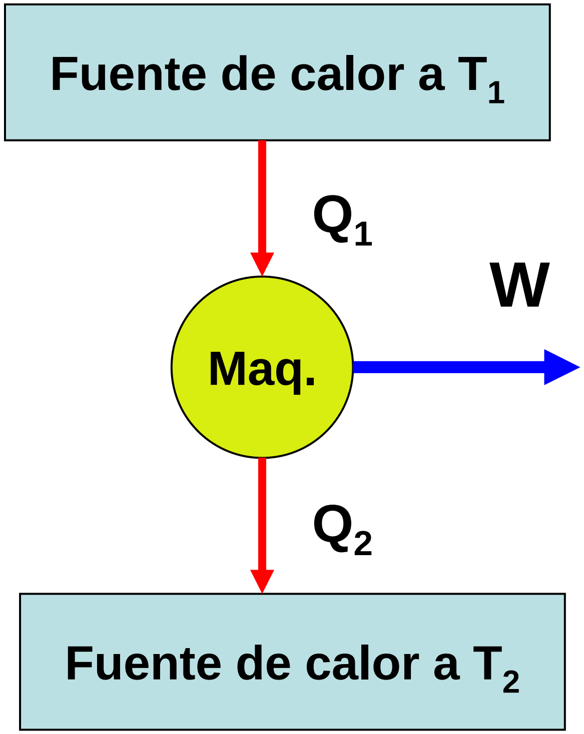
$$2H\ (g) + 2O\ (g) \qquad \Delta H^{0}_{298} = 254.33\ (Kcal/mol)$$

- **Energía enlace O – H en H_2O = 2x110.6 (Kcal/mol)**
- **Energía enlace O – O en H2O2 $\approx$ 33.19 (Kcal/mol)**

Segunda Ley de la Termodinámica

Ciclo de Carnot





Fuente de calor a T_1

Q_1

W

Maq.

Q_2

Fuente de calor a T_2

- $W_{ciclo} = - Q_{ciclo}$
- $W_{ciclo} = -(Q_1 + Q_{2)}$

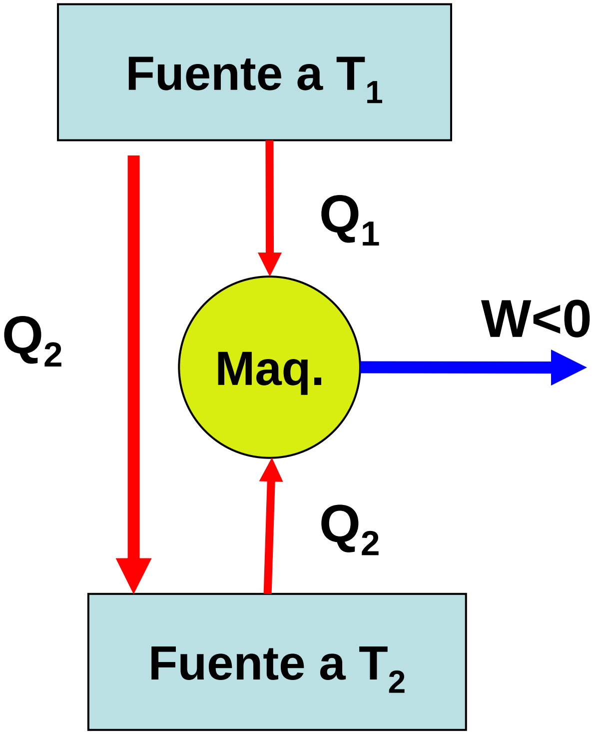
Móvil perpetuo de 1ª clase

¿Máquina conectada a una fuente única de calor? →

Siempre $W_{ciclo} \geq 0$

Si $W_{ciclo} < 0$ deben haber dos fuentes a $T_1 > T_2$

Móvil perpetuo de 2ª clase



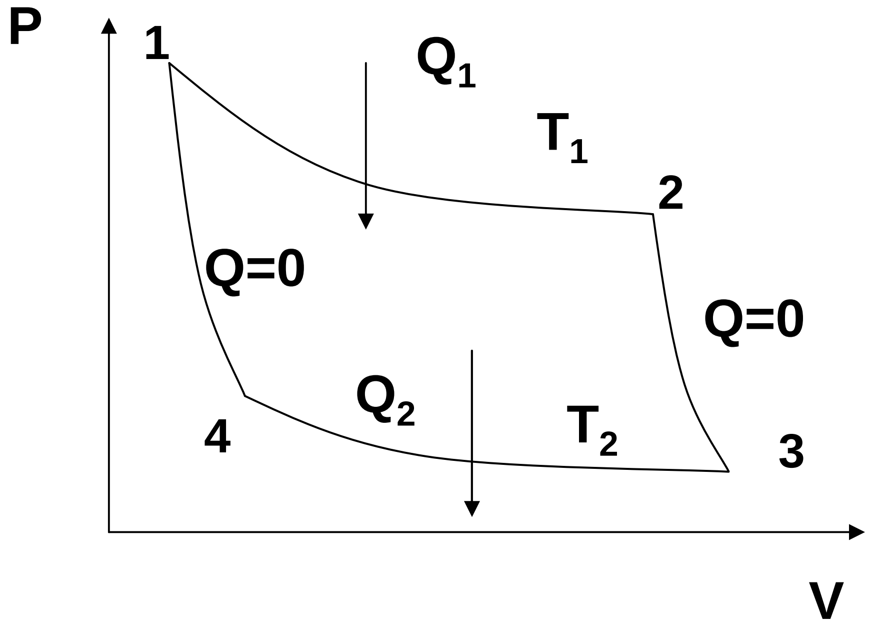
Q_1 y Q_2 difieren en signo de otro modo $-(Q_1+Q_2) = W < 0$

(móvil perpetuo de 1ª clase)

Eficiencia:

$$\boxed{\varepsilon = \frac{-W}{Q_1} = \frac{Q_1 + Q_{`2}}{Q_1} = 1 + \frac{Q_{`2}}{Q_1}}$$

Ciclo de Carnot de un gas ideal



$$W_{isotermal} = -RT\,ln\left(\frac{V_f}{V_i}\right)$$

$$W_{adiabático} = C_V\,(T_f - T_i\,)$$

en una adiabática

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}$$

$$W_{ciclo} = -RT_1\,ln\left(\frac{V_2}{V_1}\right) + RT_2\,ln\left(\frac{V_3}{V_4}\right) = R\left(T_2 - T_1\right)ln\left(\frac{V_2}{V_1}\right)$$

$$W_{ciclo} = R(T_2 - T_1) ln\left(\frac{V_2}{V_1}\right) \qquad Q_1 = RT_1 \, ln\left(\frac{V_2}{V_1}\right)$$

$$\rightarrow \quad \varepsilon = \frac{-W}{Q_1} = 1 - \frac{T_2}{T_1} \quad \rightarrow \quad \varepsilon = 1 \;\; sii \begin{cases} T_2 = 0 \\ T_1 = \infty \end{cases}$$

Imposible!

ENTROPÍA

Máquina térmica “reversible” entre T_1 y T_2

$$\oint \frac{d'Q_{rev}}{T} = 0$$

$$\varepsilon = 1 + \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1} \quad \rightarrow \quad \frac{Q_1}{T_1} + \frac{Q_2}{T_2} + = 0$$

$$\boxed{\frac{d'Q_{rev}}{T} = dS}$$

i) Máquina-1 de Carnot (reversible)

$$\begin{cases} \oint d'Q_1 = -W_1 \\ \oint \dfrac{d'Q_1}{T} = 0 \end{cases}$$

ii) Máquina-2 (irreversible)

$$\begin{cases} \oint d'Q_2 = -W_2 \\ \oint \dfrac{d'Q_2}{T} > 0 \end{cases}$$

Suponer!!

iii) Fabricar Máquina compuesta:

$$\begin{cases} -W_C = -(W_1 + W_2) = \oint (d'Q_1 + d'Q_2) = \oint d'Q_C \\ \oint \dfrac{(d'Q_1 + d'Q_2)}{T} = \oint \dfrac{d'Q_C}{T} > 0 \end{cases}$$

iv) Ajustar Máquina de Carnot para que:

$$W_C = 0 \quad \rightarrow \quad \oint d'Q_C = 0$$

$$\rightarrow \quad \begin{cases} Q_1 + Q_2 + Q_3 + \ldots = 0 \\ \\ \dfrac{Q_1}{T_1} + \dfrac{Q_2}{T_2} + \dfrac{Q_3}{T_3} + \ldots > 0 \end{cases}$$

Imposible!

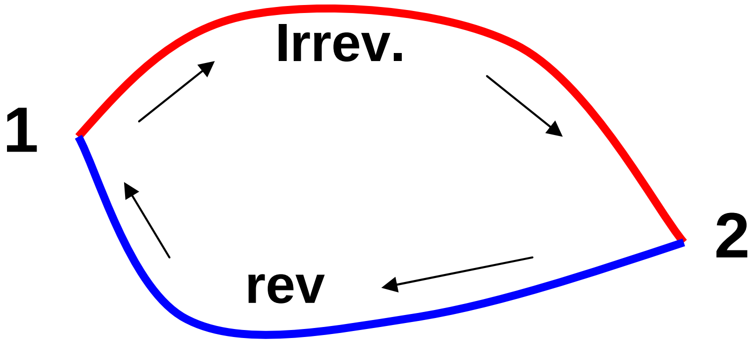
$\Rightarrow$ Extraer calor de una fuente a baja temperatura y llevarla a otra a T mayor

Para cualquier máquina:

$$\boxed{\oint \frac{d'Q}{T} \leq 0}$$

Clausius

Considerar el proceso:



$$\boxed{dS > \frac{d'Q_{irrev}}{T}}$$

Sistema aislado: $d'Q_{irrev} = 0 \quad \rightarrow \quad dS > 0$

Transformación isotermal (cambio de estado):

$$\Delta S_{vap} = \frac{Q_{rev}}{T_{vap}} = \frac{\Delta H_{vap}}{T_{vap}} \qquad \Delta S_{fus} = \frac{Q_{fus}}{T_{fus}} = \frac{\Delta H_{fus}}{T_{fus}}$$

Etc.

Definiciones

Capacidad Calórica Molar

$$\left.\begin{aligned} C_V &= \left(\frac{\partial E}{\partial T}\right)_V \equiv \frac{Q_V}{\Delta T} \\ C_P &= \left(\frac{\partial H}{\partial T}\right)_P \equiv \frac{Q_P}{\Delta T} \end{aligned}\right\} > 0$$

Coeficientes

Compresibilidad Isotermal

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T > 0$$

Expansión Isobárica

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$dS = \frac{d'Q_{rev}}{T} = \frac{1}{T}\left(dE + PdV\right) \quad \rightarrow \quad dE = TdS - PdV$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

(Maxwell)

Además:

$$\boxed{\frac{\alpha}{\beta} = \left(\frac{\partial P}{\partial T}\right)_V}$$

(usar regla cíclica)

ENTROPIA

$$\forall \text{Ciclo} \quad \oint \frac{d'Q_{irrev}}{T} < 0$$

$$\text{pero} \quad \oint \frac{d'Q_{rev}}{T} = 0 = \oint dS \quad \Rightarrow \quad dS > \frac{d'Q_{irrev}}{T}$$

Entropía función de (T,V)

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV = \frac{1}{T}\left[dE + PdV\right]$$

$$\updownarrow \qquad\qquad\qquad \updownarrow$$

$$dS = \frac{C_V}{T} dT + \frac{1}{T}\left[P + \left(\frac{\partial E}{\partial V}\right)_T\right] dV$$

Para un gas ideal:

$$\mathrm{dS} = \frac{\mathrm{C_V}}{\mathrm{T}}\mathrm{dT} + \frac{\mathrm{R}}{\mathrm{V}}\mathrm{dV}$$

Cambio a V = cte.

$$dS = \int_{T_1}^{T_2} \frac{C_V}{T} dT = C_V \, ln\left(\frac{T_2}{T_1}\right)$$

$$\left(\frac{\partial S}{\partial V}\right)_T = ?$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} = \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V$$

Calcular $\left(\dfrac{\partial^2 S}{\partial V \partial T}\right)$

i)

$$\left(\frac{\partial^2 S}{\partial V\partial T}\right) = \frac{1}{T}\left(\frac{\partial C_V}{\partial V}\right) = \frac{1}{T}\left(\frac{\partial^2 E}{\partial V\partial T}\right)$$

ii)

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[P + \left(\frac{\partial E}{\partial V}\right)_T\right]$$

$$\left(\frac{\partial^2 S}{\partial T\partial V}\right) = \frac{1}{T}\left[\left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial^2 E}{\partial T\partial V}\right)\right] - \frac{1}{T^2}\left[P + \left(\frac{\partial E}{\partial V}\right)_T\right]$$

$$\longrightarrow \quad \frac{1}{T}\left[P + \left(\frac{\partial E}{\partial V}\right)_T\right] = \left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\beta} = \left(\frac{\partial S}{\partial V}\right)_T$$

$$\boxed{\forall\ Sustancia: \quad dS = \frac{C_V}{T}dT + \frac{\alpha}{\beta}dV}$$

Entropía función de (T,P)

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP = \frac{1}{T}\left[dE + PdV\right]$$

$$dS = \frac{C_P}{T}dT + \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]dP$$

$$\left(\frac{\partial S}{\partial P}\right)_T = ?$$

i)

$$\left(\frac{\partial^2 S}{\partial P \partial T}\right) = \frac{1}{T}\left(\frac{\partial C_P}{\partial P}\right)_T = \frac{1}{T}\left(\frac{\partial^2 H}{\partial P \partial T}\right)$$

ii)

$$\left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]$$

$$\left(\frac{\partial^2 S}{\partial T \partial P}\right) = \frac{1}{T}\left[\left(\frac{\partial^2 H}{\partial T \partial P}\right) - \left(\frac{\partial V}{\partial T}\right)_P\right] - \frac{1}{T^2}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]$$

$$dS = \frac{C_P}{T}dT + \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right) - V\right]dP = \frac{C_P}{T}dT - \frac{1}{T}\left(T\,\frac{\partial V}{\partial T}\right)_P dP$$

$$\boxed{dS = \frac{C_P}{T}dT - \alpha V\,dP}$$

Para un gas ideal

$$dS = \frac{C_P}{T}dT - \frac{R}{P}dP = \frac{C_V}{T}dT + \frac{R}{V}dV$$

Entropía Absoluta:

$$\mathbf{S^0_T = \int_0^{T_F} \frac{C^0_P(s)}{T}\,dT + \frac{\Delta H^0_{Fus}}{T_{Fus}} + \int_{T_F}^{T_{Vap}} \frac{C^0_P(l)}{T}\,dT + \frac{\Delta H^0_{Vap}}{T_{Vap}} + \int_{T_{Vap}}^{T} \frac{C^0_P(g)}{T}\,dT}$$

Entropía de Reacción

$$\mathbf{\Delta S^0_{Rxn} = \sum_{Prod} \nu_{Prod}\,\overline{S}^0_{Prod} - \sum_{Reac} \nu_{Reac}\,\overline{S}^0_{Reac}}$$

Entropía de Reacción a otra Temperatura

$$\mathbf{\Delta S^0_{Rxn}(T) = \Delta S^0_{Rxn}(T_0) + \int_{T_0}^{T} \frac{\Delta C^0_P}{T}\,dT}$$

Fórmula	Nombre	M (g/mol)	$\Delta H°_f$ (kJ/mol)	$\Delta G°_f$ (kJ/mol)	$S°_f$ (J/mol K)	$C_{p,m}°$ (J/mol K)
Aluminio						
$Al_{(s)}$	aluminio	26.98	0	0	28.30	24.31
$Al_{(l)}$	aluminio	26.98	10.56	7.20	39.55	24.21
$Al_2O_{3\,(s,\,\alpha)}$	óxido de aluminio	101.96	-1675.70	-1582.30	50.92	79.04
$AlCl_{3\,(g)}$	cloruro de aluminio	133.24	-704.20	-608.80	110.67	91.84
Argón						
$Ar_{(g)}$	argón	39.94	0	0	154.84	20.79
Antimonio						
$Sb_{(s)}$	antimonio	121.75	0	0	45.69	25.23
$SbH_{3\,(g)}$	estibina	124.77	145.11	147.75	232.78	41.05
Arsénico						
$As_{(s,\,\alpha)}$	arsénico	74.92	0	0	35.10	24.64
$As_{(g)}$	arsénico	74.92	302.50	261.00	174.21	20.79
$As_{4\,(g)}$	arsénico	299.69	143.90	92.40	314.00	
$AsH_{3\,(g)}$	arsina	77.95	66.44	68.93	222.78	38.07
Azufre						
$S_{(s,\,\alpha)}$	azufre (rómbico)	32.06	0	0	31.80	22.64
$S_{(s,\,\beta)}$	azufre (monoclínico)	32.06	0.33	0.10	32.60	23.60
$S_{(g)}$	azufre	32.06	278.81	238.25	167.82	23.67
$S_{2\,(g)}$	azufre	64.13	128.37	79.30	228.18	32.47
$S_{8\,(g)}$	azufre	256.53	102.30	49.70	430.90	23.67
$SO_{2\,(g)}$	dióxido de azufre	64.06	-296.83	-300.19	248.22	39.87
$SO_{3\,(g)}$	trióxido de azufre	80.06	-395.72	-371.06	256.76	50.67
$H_2SO_{4\,(l)}$	ácido sulfúrico	98.08	-813.99	-690.00	156.90	138.90
$H_2SO_{4\,(ac)}$	ácido sulfúrico	98.08	-909.27	-744.53	20.10	
$H_2S_{(s)}$	sulfuro de hidrógeno	34.08	-20.63	-33.56	205.79	34.23
$H_2S_{(ac)}$	sulfuro de hidrógeno	34.08	-39.70	-27.83	121.00	
$SF_{6\,(g)}$	hexafluoruro de azufre	146.05	-1209.00	-1105.30	291.82	97.28
Bario						
$Ba_{(s)}$	bario	137.34	0	0	62.80	28.07
$Ba_{(g)}$	bario	137.30	180.00	146.00	170.24	20.79
$BaCO_{3\,(s)}$	carbonato de bario	197.33	-1216.30	-1137.60	112.10	85.40
$BaSO_{4\,(s)}$	sulfato de bario	233.39	-1473.19	-1362.3	132.20	101.75
$BaO_{(s)}$	óxido de bario	153.34	-553.50	-525.10	70.43	47.78

Espontaneidad ⇔ Equilibrio

$$1^{era}\ Ley: \qquad TdS \geq dE - d'W$$

Luego: $$\boxed{-dE - P_{ext}dV + d'U + TdS \geq 0}$$

Cambio Isotermal:

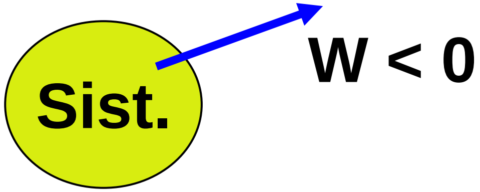
$$-\mathrm{dE} + \mathrm{d(TS)} \geq -\mathrm{d'W}$$

$$-\mathrm{d(E - TS)} = -\mathrm{dA} \geq -\mathrm{d'W}$$

$$\boxed{\mathrm{A = E - TS}}$$

Energía Libre de Helmholtz

Proceso a (T,P) = Ctes.



$$Si \quad P = P_{sist}$$

$$-\left[dE + d(PV) - d(TS)\right] \ge -d'U$$

O bien: $\boxed{-dG \ge -d'U}$

Energía Libre de Gibbs:

$$\mathrm{G = E + PV - TS = H - TS = A + PV}$$

Sólo Trabajo Volumétrico

$$\mathrm{d'U = 0 \quad \Rightarrow \quad -dG \ge 0 \quad o \qquad dG \le 0}$$

ΔG = Fuerza Motriz en la Naturaleza

$$\mathrm{\Delta G = \Delta H - T\Delta S}$$

(T= cte)

Relaciones útiles

$$dE = TdS - PdV \quad \Rightarrow \quad \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

(Maxwell)

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1$$

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{1}{\alpha V}\right)_P (-\beta V)_T = -1$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\alpha}{\beta}\right)$$

Ecuaciones Fundamentales

$$\left.\begin{array}{l} dE = TdS - PdV \\ dH = TdS + VdP \\ dA = -SdT - PdV \\ dG = -SdT + VdP \end{array}\right\} \leftrightarrow \left\{\begin{array}{l} \left(\dfrac{\partial T}{\partial V}\right)_S = -\left(\dfrac{\partial P}{\partial S}\right)_V \\ \left(\dfrac{\partial T}{\partial P}\right)_S = \left(\dfrac{\partial V}{\partial S}\right)_P \\ \left(\dfrac{\partial S}{\partial V}\right)_T = \left(\dfrac{\partial P}{\partial T}\right)_V \\ -\left(\dfrac{\partial S}{\partial P}\right)_T = \left(\dfrac{\partial V}{\partial T}\right)_P \end{array}\right.$$

Ecuación de Estado Termodinámica

$$dE = TdS - PdV$$

$$\boxed{P = T\left(\frac{\partial P}{\partial T}\right)_V - \left(\frac{\partial E}{\partial V}\right)_T}$$

$$dH = TdS + VdP$$

$$\boxed{V = T\left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial H}{\partial P}\right)_T}$$

además $\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\beta}$

$$\boxed{\text{i)}\quad \left(\frac{\partial E}{\partial V}\right)_T = \frac{\alpha T - \beta P}{\beta}}$$

$$\boxed{\text{ii)}\quad \left(\frac{\partial H}{\partial P}\right)_T = V(1 - \alpha T)}$$

Luego:

$$dE = C_V dT + \frac{(\alpha T - \beta P)}{\beta} dV$$

$$dH = C_P dT + V(1 - \alpha T) dP$$

$$C_P - C_V = \left[P + \left(\frac{\partial E}{\partial V} \right)_T \right] V\alpha = \frac{TV\alpha^2}{\beta}$$

$$C_P \mu_{JT} = -\left(\frac{\partial H}{\partial P} \right)_T = V(\alpha T - 1)$$

Propiedades de G

$$dG = -SdT + VdP$$

1) Variación de G con la presión (T=cte)

$$\overline{G}(T,P) = \overline{G}^{0}(T) + \int_{1.0}^{P} \overline{V}dP$$

i) Para Líquidos y sólidos:

$$\overline{V} \approx cte \qquad \overline{G}(T,P) = \overline{G}^{0}(T) + \overline{V}(P-1)$$

ii) Para Gases Ideales:

$$\overline{G}(T,P) = \overline{G}^0(T) + RT\ln P$$

$$\boxed{\mu(T,P) = \mu^0(T) + RT\ln P}$$

Donde: $\mu = \overline{G} = \frac{G}{n}$

(Potencial Químico)

○

ii) Para Gases Reales: **Inventar funcionalidad f**

$$\mu(T,P) = \mu^0(T) + RT\ln f$$

f = “Fugacidad”

$$d\mu = \overline{V}dP$$

$$d(\mu - \mu_{ideal}) = (\overline{V} - \overline{V}_{ideal})dP$$

→ integrar

$$(\mu - \mu_{ideal}) - (\mu^{*} - \mu^{*}_{ideal}) = \int_{P^{*}}^{P} (\overline{V} - \overline{V}_{ideal})dP$$

Si p* → 0

$$(\mu^{*} \rightarrow \mu^{*}_{ideal})$$

$$(\mu - \mu_{ideal}) = \int_{0}^{P} (\overline{V} - \overline{V}_{ideal})dP$$

o bien:

$$RT(\ln f - \ln P) = \int_{0}^{P} (\overline{V} - \overline{V}_{ideal})dP$$

$$\ln f = (\ln P) + \frac{1}{RT}\int_{0}^{P} (\overline{V} - \overline{V}_{ideal})dP$$

Donde la “fugacidad” f :

$$\ln f = \ln P + \int_0^P \frac{Z-1}{P}\,dP$$

2) Variación de G con la Temperatura (P=cte)

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \qquad \rightarrow \qquad \frac{\partial\left(\frac{G}{T}\right)}{\partial T} = -\frac{H}{T^2}$$

Ecuación de Gibbs - Helmholtz