Formulario Termodinámica

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Interpolación

$$\frac{x-x_1}{x_1-x_2} = \frac{y-y_1}{y_1-y_2}$$

} Tablas

$PV = nRT$

x = Calidad de vapor

$$x = \frac{v - v_f}{v_g - v_f}$$

$v = v_f + x(v_g - v_f)$

$u = u_f + x(u_g - u_f)$

$h = h_f + x h_{fg}$

$s = s_f + x s_{fg}$

Trabajo

Proceso Isotérmico $W = nRT \ln\left(\frac{V_2}{V_1}\right)$

Proceso Isobárico $W = P(V_2 - V_1)$

Proceso Isocórico $W = 0$ $\left(\frac{P_1}{T_1} = \frac{P_2}{T_2}\right)$

Proceso Politrópico $W = \frac{K}{1-n}\left(V_2^{1-n} - V_1^{1-n}\right)$ $(PV^n = K)$

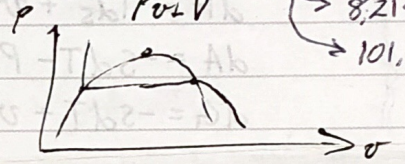
$$R = 8{,}314 \frac{Pa \cdot m^3}{mol \cdot K} = 10{,}73 \frac{psia \cdot ft^3}{lbmol\, R}$$

$\rightarrow 0{,}0821 \frac{atm \cdot L}{mol \cdot K}$

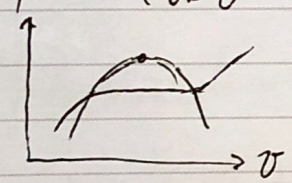
$\rightarrow 8{,}21 \cdot 10^{-5} \frac{atm \cdot m^3}{mol \cdot K}$

$\rightarrow 101{,}3\ J$

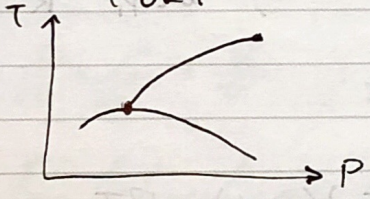
P vs V



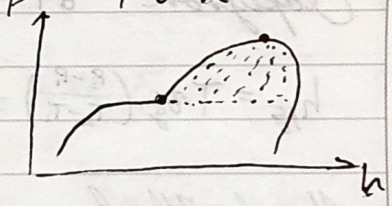
T vs V



T vs P



P vs h



P: $1\,atm = 101325\,Pa = 101{,}325\,KPa = 760\,mmHg = 1{,}033 \frac{Kg}{cm^3} = 1{,}01325\,bar = 14{,}7\,psia$

T: $T_K = T_{°C} + 273{,}15$; $T_{°F} = 1{,}8\,T_{°C} + 32$; $T_R = T_{°F} + 459{,}67$; $1K = 1{,}8R$

M: $1Kg = 2{,}205\,lb$; $1m^3 = 35{,}315\,ft^3$; $1cal = 0{,}00397\,BTU$; $1g = 0{,}0022\,lbm$

$1g\,mol = 0{,}0022046\,lb\,mol$; $1m = 3{,}2808\,ft$; $1\,BTU = 5{,}40395\,psia \cdot ft^3$

$1 \frac{lb}{lb\,mol} = 1 \frac{g}{g\,mol} = 1 \frac{Kg}{Kg\,mol}$

v: $1 \frac{m^3}{Kg} = 16{,}018 \frac{ft^3}{lb}$ $1\,psi = 6894{,}7\,Pa$

$1cal = 4{,}184\,J$ $1\,BTU = 0{,}29307\,Watt$

Sistema Abierto

$\Delta E_p + \Delta E_c + \Delta H = Q - W$

Sistema Cerrado

$\Delta E_p + \Delta E_c + \Delta U = Q - W$

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$$\Delta E_p = \frac{m \cdot g \cdot \Delta h}{g_c} \qquad m = G_m \qquad g = 9{,}81\ m/s^2 = 32{,}2\ ft/s^2$$

$$g_c = 1\ \frac{kg\,m}{N s^2} = 32{,}2\ \frac{ft\,lbm}{lbf\,s^2}$$

$$\Delta E_c = \frac{1}{2}\,\frac{m(V_2^2 - V_1^2)}{g_c}$$

$$\Delta H = \int_{T_1}^{T_2} c_p\, dT \qquad c_p = a + bT + cT^2 + dT^3 \qquad c_p = a + bT + \frac{c}{T^2} \qquad \left[\frac{kJ}{kg\,mol\,°K}\right]$$

$$c_p \equiv \left(\frac{\delta q}{dT}\right)_p \qquad c_v \equiv \left(\frac{\delta q}{dT}\right)_v$$

$$\Delta U = \int_{T_1}^{T_2} c_v\, dT \ ; \quad \Delta U = U_2 - U_1 \ ; \quad \Delta U = Q - W \ ; \quad \Delta U = \Delta H - \Delta P v$$

$G_{m_1} = G_{m_2}$ y $G_{v_1} = G_{v_2}$ (líquidos) — $G_{m_1} = G_{m_2}$ y $G_{v_1} \neq G_{v_2}$ (gases)

$$G_m = \frac{AV}{v} \ ; \quad G_v = AV \quad \Rightarrow \quad G_m = G_v \cdot \rho$$

Tipo	Ecuaciones fundamentales	Maxwell
Energía interna	$dU = Tds - Pdv$	$\left(\frac{\delta T}{\delta v}\right)_s = -\left(\frac{\delta P}{\delta s}\right)_v$
Entalpía	$dH = Tds + vdP$	$\left(\frac{\delta T}{\delta P}\right)_s = \left(\frac{\delta v}{\delta s}\right)_P$
Helmholtz	$dA = -SdT - Pdv$	$\left(\frac{\delta s}{\delta v}\right)_T = \left(\frac{\delta P}{\delta T}\right)_v$
Gibbs	$dG = -SdT + vdP$	$-\left(\frac{\delta s}{\delta P}\right)_T = \left(\frac{\delta v}{\delta T}\right)_P$

Clapeyron $\quad \frac{dP}{dT} = \frac{h_{fg}}{T v_{fg}} \ ; \quad \ln\frac{P_2}{P_1} = \frac{h_{fg}}{R}\left[\frac{T_2 - T_1}{T_1 \cdot T_2}\right]$ · PM · Conversión $\frac{BTU}{psia}$

$$h_{fg} = T v_g \left(\frac{P_2 - P_1}{T_2 - T_1}\right)$$ · conv. $\frac{BTU}{psia}$

Van der Waals $\quad \left(P + \frac{a}{v^2}\right)(v - b) = RT$ · $\{ v \cdot PM$

$$a = \frac{27}{64}\,\frac{R^2 T_c^2}{P_c} \ ; \quad b = \frac{1}{8}\,\frac{R T_c}{P_c}$$

Beattie-Bridgeman $\quad P = \frac{RT}{v^2}\left(1 - \frac{c}{vT^3}\right)(v + B) - \frac{A}{v^2}$ $\quad \{ R : PM$

$$A = A_0\left(1 - \frac{a}{v}\right) \ ; \quad B = B_0\left(1 - \frac{b}{v}\right) \qquad \{ A : 1000$$

Redlich Kwong $\quad P = \frac{RT}{v - b} - \frac{a}{T^{1/2} v(v + b)}$

$$a = 0{,}42748\,\frac{R^2 T_c^{2,5}}{P_c} \ ; \quad b = 0{,}08664\,\frac{R T_c}{P_c}$$

Soave-Redlich Kwong $\quad P = \frac{RT}{v - b} - \frac{a'\lambda}{v(v + b)}$

$$a' = 0{,}42748\,\frac{R^2 T_c^2}{P_c} \ ; \quad b = 0{,}08664\,\frac{R T_c}{P_c} \ ; \quad \lambda = \left[1 + K\left(1 - T_r^{1/2}\right)\right]^2 \ ; \quad K = (0{,}48 + 1{,}574\omega - 0{,}176\omega^2)$$

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Peng-Robinson $P = \frac{RT}{v-b} - \frac{a\alpha}{v(v+b)+b(v-b)}$

$a = 0{,}45724 \frac{R^2 T_c^2}{P_c}$; $b = 0{,}0778 \frac{RT_c}{P_c}$; $\alpha = \left[1 + K(1 - T_r^{1/2})\right]^2$; $K = 0{,}37464 + 1{,}54226\omega - 0{,}26992\omega^2$

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Correlaciones Generalizadas

$$Z = \frac{Pv}{RT}$$

$T_r = \frac{T}{T_c}$; $P_r = \frac{P}{P_c}$; $v_r = \frac{v}{v_c}$

Redlich Kwong $Z = \frac{1}{1-h} - \frac{4{,}9340}{T_r^{1.5}}\left(\frac{h}{1+h}\right)$ $\quad$ $*\, Z_u - Z_{pu} = 0{,}0001$

$h = \frac{0{,}08664\, P_r}{Z\, T_r}$

Pitzer $Z = 1 + B^0 \frac{P_r}{T_r} + \omega B' \frac{P_r}{T_r}$

$B^0 = 0{,}083 - \frac{0{,}422}{T_r^{1.6}}$; $B' = 0{,}139 - \frac{0{,}172}{T_r^{4.2}}$

Lee Kesler $Z = Z^0 + \omega Z'$ $\quad$ ω, Z^0 y $Z' \rightarrow$ tablas

Correlaciones Para Líquidos

Rackett $v^{sat} = v_c Z_c^{(1-T_r)^{0.2857}}$

Lydersen, Greenkorn $\rho_r = \frac{\rho}{\rho_c} = \frac{v_c}{v}$; $v_2 \rho_{r_2} = v_1 \rho_{r_1}$

Efectos Caloríficos

Sensible: $Q = \Delta H = \int_{T_1}^{T_2} C_p\, dT$ $\quad$ $C_p = a + bT + cT^2 + dT^3$ ó $a + bT + \frac{c}{T^2}$ $\left[\frac{J}{mol\,K}\right]$

Latente: $Q = \Delta H_T = \int_{T_1\,K}^{T_2\,K} C_{p(l)}\, dT + \Delta H_{vap} + \int_{T_1\,°C}^{T_2\,°C} C_{p(g)}\, dT$ $\quad$ K → Líquidos, °C → Gases

*Cuando $P \neq 1$ atm

Ec. de Antoine (P y T saturación) $\ln P^{sat} = A - \frac{B}{C+T}$ $\quad$ *(Apéndice G₁ → A, B, C) P.78 *(P en mm de Hg)

Ec. de Watson (h_{fg} → calor de vaporización) $\frac{\Delta H_{vap_2}}{\Delta H_{vap_1}} = \left(\frac{1-T_{r_2}}{1-T_{r_1}}\right)^{0.38}$ $\quad$ ($T = T_{eb}$)

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Calor de Reacción

A condiciones estándar (1 atm y 25°C o 298,15K):

$$Q = \Delta H^\circ_{RXN} = \sum n_i \Delta H^\circ_{f_i} - \sum n_j \Delta H^\circ_{f_j}$$

i = productos
j = reactivos

$\Delta H < 0 \rightarrow$ Exotérmica
$\Delta H > 0 \rightarrow$ Endotérmica

A condiciones NO Estándar:

$$Q = \sum n_i \left[\Delta H^\circ_{f_i} \int_{25°C}^{T_{eb}} c_{p_i} dT + \Delta H_{vap_i} + \int_{T_{eb}}^{T_2} c_{p_i} dT\right] - \sum n_j \left[\Delta H^\circ_{f_j} + \int_{25°C}^{T_{eb}} c_{p_j} dT + \Delta H_{vap_j} + \int_{T_{eb}}^{T_f} c_{p_j} dT\right]$$

Calor de Sistemas Multicomponentes

$$Q = G_{n_T} \left[\sum x_i \left(\int_{T_1}^{T_{eb}} c_p dT + \Delta H_{vap} + \int_{T_{eb}}^{T_2} c_p dT\right)\right]$$

Entropía

A condiciones Estándar

$$\Delta S^\circ_{universo} = \Delta S^\circ_{sistema} + \Delta S^\circ_{entorno}$$

$$\Delta S^\circ_{sistema} = \sum n \Delta S^\circ_{productos} - \sum n \Delta S^\circ_{reactivos}$$

$$\Delta S^\circ_{entorno} = \frac{-\Delta H^\circ_{sistema}}{T} \qquad \Delta H^\circ_{sistema} = \Delta H^\circ_{RXN}$$

Energía Libre de Gibbs

$G = H - TS$

$$\Delta G^\circ_{RXN} = \sum n_i \Delta G^\circ_{f_i} - \sum n_j \Delta G^\circ_{f_j}$$

$\Delta G = (-) \rightarrow$ Espontáneo
$\Delta G = (+) \rightarrow$ No Espontáneo

Eficiencia $\eta = \frac{W}{Q_H}$ $\qquad Q_H = W + Q_c \qquad \eta = 1 - \frac{Q_c}{Q_H} = 1 - \frac{T_c}{T_H}$

Q_H = Calor Suministrado; Q_c = Calor disipado

Desigualdad de Clausius $\oint \frac{dQ}{T} \leq 0 \qquad \sum_{i=1}^{n} \frac{Q_i}{T_i} \leq 0$

Ciclo de Refrigeración: Compresión $\rightarrow$ (SA) isoentrópico ($\Delta S = 0$); condensación $\rightarrow$ (SA) isobárico; expansión $\rightarrow$ (SC) adiabático ($\Delta H = 0$); evaporación $\rightarrow$ (SA) isobárico

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Energy Balance Formulary

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Unit Conversions

$S.G. = \frac{\rho_{substance}}{\rho_{reference}} \rightarrow (H_2O @ 4°C = 1 g/cm^3)$

P: $1 atm = 101325 Pa = 760 mm Hg = 1,033 \frac{Kg}{cm^3} = 1,01325 bar = 14,7 psia$

T: $T_K = T_{°C} + 273,15$; $T_{°F} = 1,8 T_{°C} + 32$; $T_R = T_{°F} + 459,67$; $1K = 1,8 R$

m: $1 Kg = 2,2046 lb$; $1 g = 0,002046 lb$; $1 \frac{lb}{lb\,mol} = 1 \frac{g}{g\,mol} = 1 \frac{Kg}{Kg\,mol}$; $1 m^3 = 1000 L$

V: $1 m^3 = 35,315 ft^3$; **v:** $1 \frac{m^3}{Kg} = 16,018 \frac{ft^3}{lb}$; **l:** $1 m = 3,2808 ft = 39,370 in$

E: $1 cal = 4,184 J = 0,00397 BTU$; $1 BTU = 5,40395 psia \cdot ft^3$

Ecuaciones de Energía

Sistema abierto: $\Delta E_p + \Delta E_K + \Delta H = Q - W$

Sistema cerrado: $\Delta E_p + \Delta E_K + \Delta U = Q - W$

$\Delta U = \int_{T_1}^{T_2} C_v \, dT$ $\quad \Delta H = \int_{T_1}^{T_2} C_p \, dT$ $\quad C_p = a + bT + cT^2 + dT^3$ $\left[\frac{KJ}{Kg\,mol\,°K}\right]$

or $C_p = a + bT + \frac{c}{T^2}$

$\Delta H = \Delta U + \Delta P v$

$\Delta E_p = mg\Delta h$

$\Delta E_K = \frac{1}{2} m (V^2 - V_0^2)$

Processes with Several Streams

$Q + W = \sum_{out} E_i - \sum_{in} E_i$ $\quad E_i = U_i + E_{K_i} + E_{P_i}$ (H_i)

$\Delta E_K = \sum_{out} \frac{1}{2} m_i V_i^2 - \sum_{in} \frac{1}{2} m_i V_i^2$ $\quad \Delta H = \sum_{out} m_i \hat{H}_i - \sum_{in} m_i \hat{H}_i$ $\quad \Delta E_P = \sum_{out} m_i g h_i - \sum_{in} m_i g h_i$

Energy Balance in Unsteady State

Transfer: $\Delta E_T = \Delta U + \Delta E_K + \Delta E_P$ $\quad \Delta t (Q + W) = \int_{t_1}^{t_2} \frac{dU}{dt} + \int \frac{dE_K}{dt} + \int \frac{dE_P}{dt}$

* Note: E_K and $E_P \approx 0$; No RXN ; No phase change ; $\hat{H}$ and $\hat{U}$ are independent of P
C_v and C_p are independent of composition and T

Open System: $m \cdot C_p \cdot \frac{dT_{sys}}{dt} = m \cdot C_p (T_{in} - T_{sys}) + Q - W$

Closed System: $m \cdot C_v \cdot \frac{dT_{sys}}{dt} = Q + W$

Energy Balance in Reactive Systems

Heat of RXN Method *(for only 1 reaction)

$$Q = \Delta H = \sum_{out} n_i \hat{H}_i - \sum_{in} n_i \hat{H}_i + \underbrace{n_A \cdot \frac{\Delta H^\circ_{RXN}}{\nu_A}}_{\xi \Delta H^\circ_r = \text{Extent of RXN}}$$

n_A = moles de compuesto limitante en el proceso

ν_A = coeficiente estequiométrico del compuesto limitante en RXN

$$\Delta H^\circ_{RXN} = \sum_{products} n_i H^\circ_f - \sum_{reactants} n_i H^\circ_f$$

$$\hookrightarrow = \sum_{reactants} n_i H^\circ_c - \sum_{products} n_i H^\circ_c$$

* Reference State: 25 °C; 1 atm; Phase state of compounds in RXN

Heat of Formation Method

$$Q = \Delta H = \sum_{out} n_i \hat{H}_{if} - \sum_{in} n_i \hat{H}_{if}$$

* Reference State: 25 °C; 1 atm; Phase of Elements

$$\hat{H}_{i\,compounds} = \Delta H^\circ_f + \int_{T_1}^{T_2} c_p \, dt$$

Fuels Heating Values

- High or Gross Heating Value (HHV)

$$HHV = LHV + n_w \Delta \hat{H}_v (H_2O, 25°C)$$

$HHV = -(\Delta H^\circ_c)$ con $H_2O_{(v)}$ as product

$\Delta H_v(H_2O, 25°C) = 44{,}013 \frac{KJ}{mol}$ or $18934 \frac{BTU}{lb\,mol}$

- Low Heating Value (LHV)

$$LHV = HHV - n \Delta H_v (H_2O, 25°C)$$

- Heating Value of Mixes

$$\underbrace{HV}_{LHV \text{ or } HHV} = \sum x_i \underbrace{(HV)_i}_{LHV \text{ or } HHV}$$

Adiabatic Flame Temperature

* Adiabatic: $Q = \Delta H = 0$

n_f = moles of fuel

$$\sum_{out} n_i \hat{H}_i \Big|_{T_{ref}}^{T_{ad}} = -n_f \Delta H^\circ_c + \sum_{in} n_i \hat{H}_i \Big|_{T_{ref}}^{T_{in}}$$

$$\Delta H = n_f \Delta H^\circ_c + \sum_{out} n_i \hat{H}_i \Big|_{T_{ref}}^{T_{ad}} - \sum_{in} n_i \hat{H}_i \Big|_{T_{ref}}^{T_{in}}$$

Heats of Solution and Mixing

$$\Delta H_{mix} = x_A \Delta \hat{H}_A + x_B \Delta \hat{H}_B + \dots$$

$$C_{P\,mix} = x_A C_{PA} + x_B C_{PB} + \dots$$

$$q_{RXN} = -(q_{sol} + q_{cal})$$

$$q_{sol} = m_{sol} \underbrace{C_{sol}}_{\text{some or water} = 4{,}184 \, J/g°C} \Delta T$$

$$q_{RXN} = (\Delta H_{RXN})(\text{mol solt})$$

$$q_{cal} = C' \Delta T$$

$C' = 10{,}5$ J/°C for automated

$= 17{,}5$ J/°C for manual

$$\Delta H_{RXN} = -\frac{(m_{sol} C_{sol} \Delta T + C' \Delta T)}{(\text{mol solt})}$$