

TERMODINAMICA

Scambi di CALORE e LAVORO tra: SISTEMA ↔ AMBIENTE

UNIVERSO

↗ APERTO → SCAMBIA ENERGIA E MATERIA
SISTEMA → CHIUSO → SCAMBIA ENERGIA, NON MATERIA
↘ ISOLATO → NON SCAMBIA ENERGIA NE' MATERIA

SCAMBI DI CALORE → SCAMBIO DI → VARIAZIONE DI
E LAVORO ENERGIA ENERGIA INTERNA

ENERGIA INTERNA (E) → CINETICA + POTENZIALE
E → FUNZIONE DI STATO

CONVENZIONE STORICA

$Q > 0$ assorbito dal sistema $W > 0$ fatto dal sistema
 $Q < 0$ ceduto dal sistema $W < 0$ fatto sul sistema

I PRINCIPIO DELLA TERMODINAMICA

$$\Delta E = Q - W$$

$$dE = \delta Q - \delta W$$

$P = \text{costante}$ $\Delta E = Q - W = Q_p - P\Delta V$

$Q_p = \Delta E + P\Delta V = \Delta H$ $H = E + PV$

$V = \text{costante}$ $W = 0$ $\Delta E = Q_v$

ENDOTERMICO ESOTERMICO

$P = \text{cost}$ $\Delta H > 0$ $\Delta H < 0$ $\Delta H = Q_p$

$V = \text{cost}$ $\Delta E > 0$ $\Delta E < 0$ $\Delta E = Q_v$

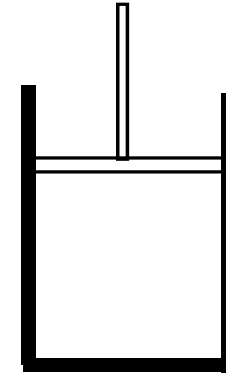
Calore specifico molare $c = \frac{dQ}{dT}$

A pressione costante $c_p = \frac{dQ_p}{dT} = \frac{dH}{dT}$

A volume costante $c_v = \frac{dQ_v}{dT} = \frac{dE}{dT}$

$c_p = \frac{dH}{dT} = \frac{d(E + PV)}{dT} = \frac{dE}{dT} + P\frac{dV}{dT} = c_v + P\frac{dV}{dT}$ $c_p > c_v$

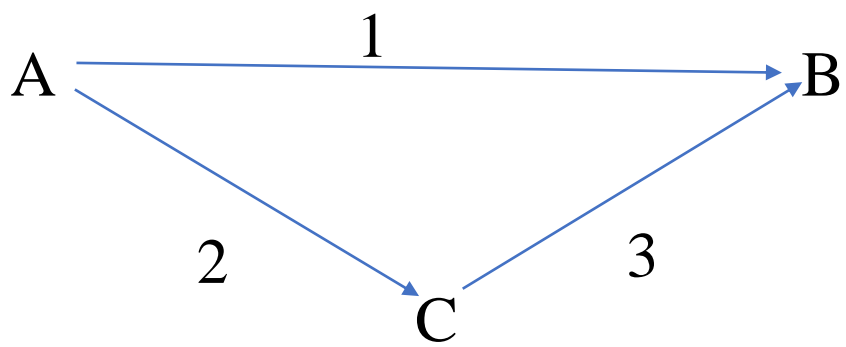
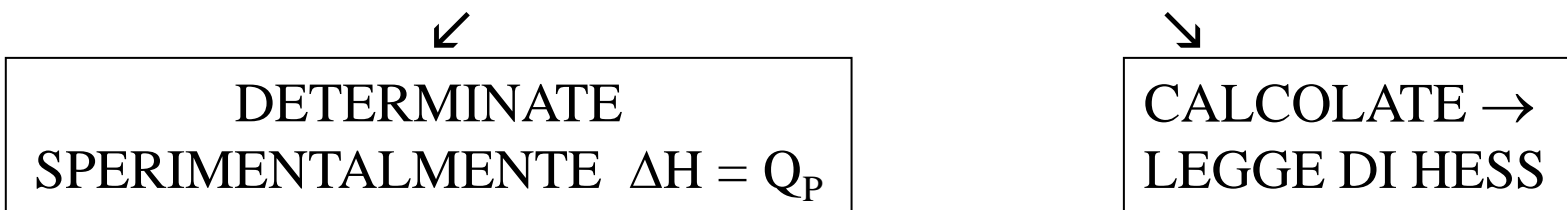
Liquidi e solidi	$\Delta V \cong 0$	$c_p \cong c_v$	$\Delta H \cong \Delta E$
gas	$V = RT/P$	$c_p = c_v + P\frac{d(RT/P)}{dT} = c_v + R$	$\Delta H = \Delta E + RT$



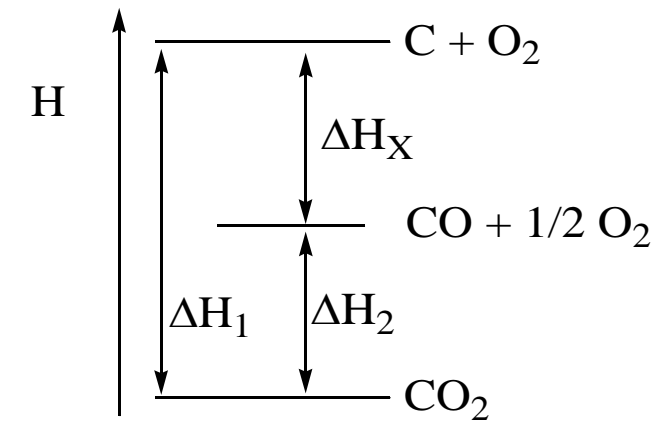
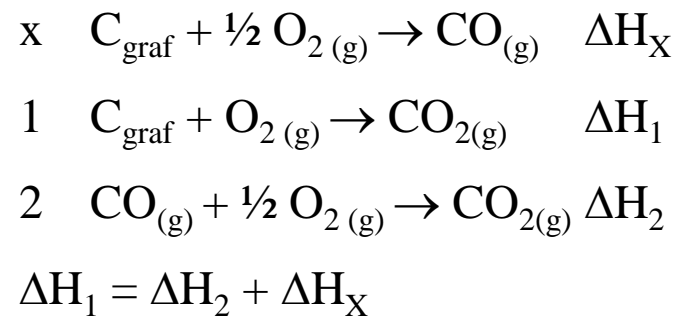
CALORI DI REAZIONE ΔH_{REAZ} DIPENDONO DA T
 CONDIZIONI STANDARD: $T = 25^\circ = 298 \text{ K}$ $P = 1 \text{ atm}$

LEGGE DI HESS \rightarrow L'ENTALPIA E' FUNZIONE DI STATO
 LA SUA VARIAZIONE: - NON DIPENDE DAL CAMMINO PERCORSO
 - DIPENDE DALLO STATO INIZIALE E FINALE

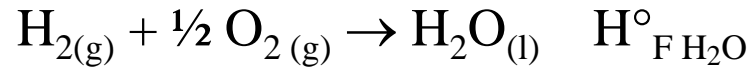
ENTALPIE DI REAZIONE



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



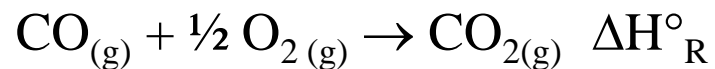
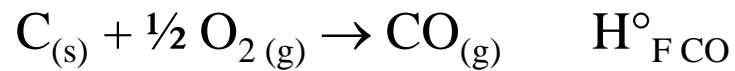
ENTALPIE STANDARD DI FORMAZIONE H°_F



$H^\circ_F = 0$ per gli ELEMENTI nel loro STATO STANDARD

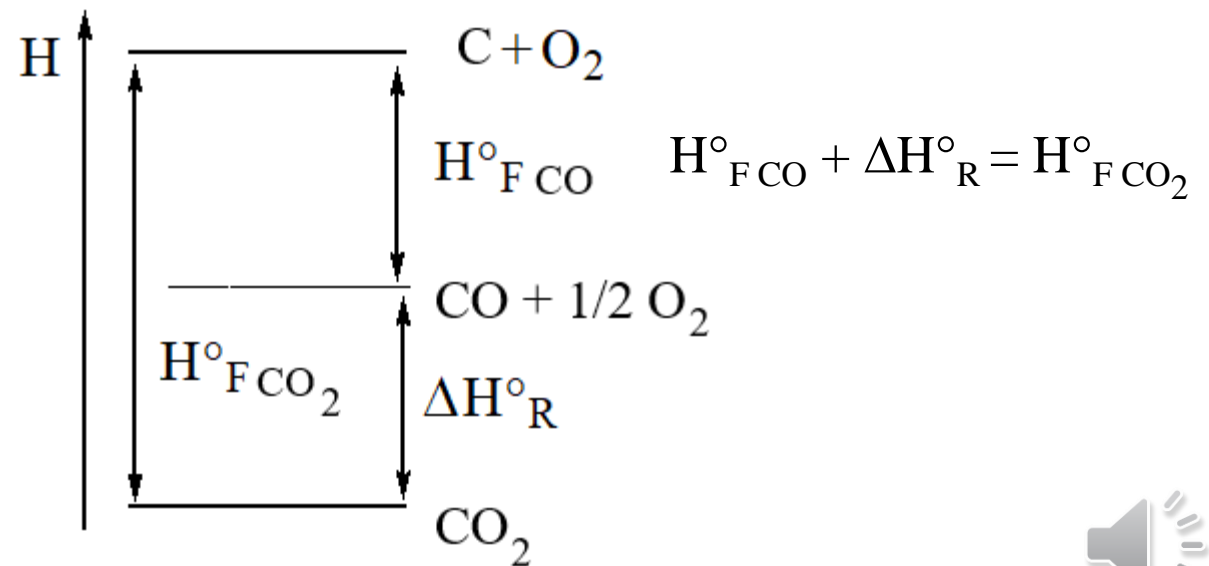
CALCOLO di ΔH° di una REAZIONE da H°_F di PRODOTTI e REAGENTI

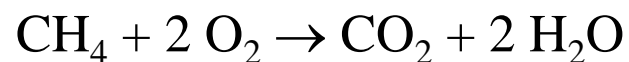
$$\Delta H^\circ_R = \sum_i v_i H^\circ_{F i} \text{ (PRODOTTI)} - \sum_i v_i H^\circ_{F i} \text{ (REAGENTI)} \quad v_i \text{ coefficiente stechiometrico}$$



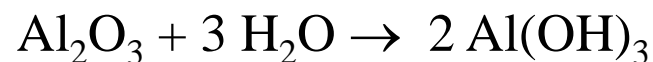
$$\Delta H^\circ_R = H^\circ_{F CO_2} - H^\circ_{F CO}$$

$$H^\circ_{F CO} = H^\circ_{F CO_2} - \Delta H^\circ_R$$

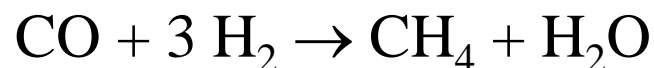




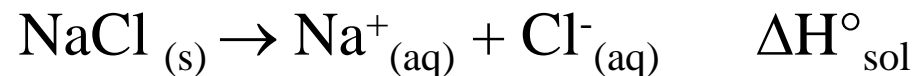
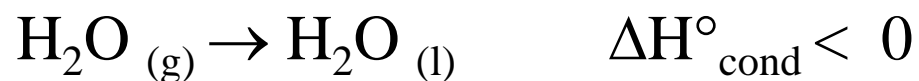
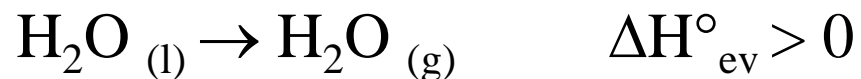
$$\Delta H^\circ_{\text{R}} = H^\circ_{\text{F CO}_2} + 2 H^\circ_{\text{F H}_2\text{O}} - H^\circ_{\text{F CH}_4}$$



$$\Delta H^\circ_{\text{R}} = 2 H^\circ_{\text{F Al}(\text{OH})_3} - 3 H^\circ_{\text{F H}_2\text{O}} - H^\circ_{\text{F Al}_2\text{O}_3}$$



$$\Delta H^\circ_{\text{R}} = H^\circ_{\text{F CH}_4} + H^\circ_{\text{F H}_2\text{O}} - H^\circ_{\text{F CO}}$$



Reazione endotermica $\Delta H^\circ_{\text{R}} > 0$



Si formano legami più deboli
di quelli che si rompono

Reazione esotermica $\Delta H^\circ_{\text{R}} < 0$

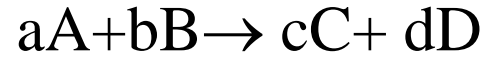


Si formano legami più forti
di quelli che si rompono

$$\Delta H = f(T) \quad c_p = \frac{\delta Q_p}{dT} = \frac{dH}{dT} \Rightarrow dH = c_p dT \quad \Delta H = \int c_p dT$$

Se $c_p = \text{costante}$

$$\Delta H = c_p \Delta T$$



$$\Delta H_{\text{Reaz}} = \sum_{\text{Prodotti}} \nu_i H_i - \sum_{\text{Reagenti}} \nu_i H_i = cH_C + dH_D - aH_A - bH_B$$

$$\frac{d\Delta H_{\text{Reaz}}}{dT} = c \frac{dH_C}{dT} + d \frac{dH_D}{dT} - a \frac{dH_A}{dT} - b \frac{dH_B}{dT} =$$

$$= c \times c_{p(C)} + d \times c_{p(D)} - a \times c_{p(A)} - b \times c_{p(B)} = \sum_{\text{Prodotti}} \nu_i c_{p_i} - \sum_{\text{Reagenti}} \nu_i c_{p_i} = \Delta c_p$$

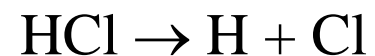
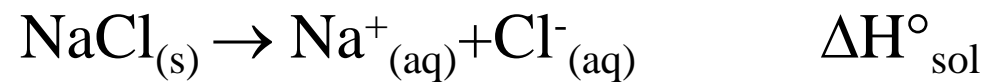
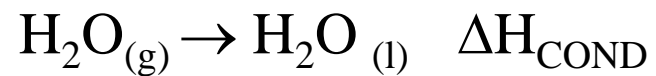
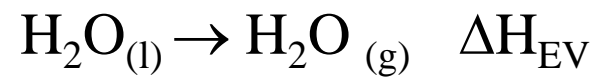
$$d\Delta H_{\text{Reaz}} = \Delta c_p dT \Rightarrow \Delta H_{\text{Reaz}(T_2)} - \Delta H_{\text{Reaz}(T_1)} = \int_{T_1}^{T_2} \Delta c_p dT$$

$$T_1 = 298 \text{ K} \Rightarrow \Delta H_{\text{Reaz}}^0$$

$$T_2 = T \Rightarrow \Delta H_{\text{Reaz}}(T)$$

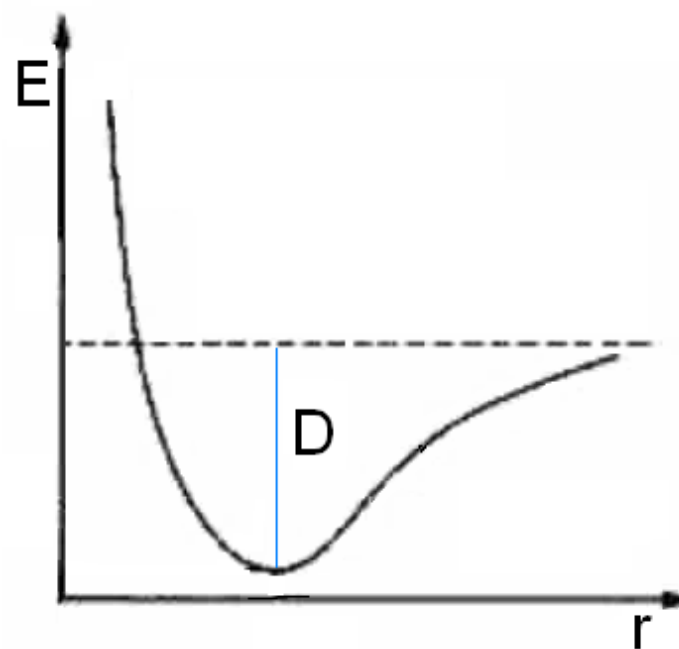
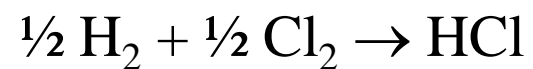
$$\Delta H_{\text{Reaz}(T)} = \Delta H_{\text{Reaz}}^0 + \int_{298}^T \Delta c_p dT \cong \Delta H_{\text{Reaz}}^0 + \Delta c_p \Delta T$$

$c_p = \text{cost}$



$$\Delta H^{\circ}_{\text{DISS}} = D > 0$$

$$\Delta H^{\circ}_{\text{DISS}} \neq -\Delta H^{\circ}_{\text{F}}$$



PRIMO PRINCIPIO DELLA TERMODINAMICA $\Delta U=Q-W$



L'energia non si crea né si distrugge ma si trasforma

CONSERVAZIONE DELL'ENERGIA



SECONDO PRINCIPIO DELLA TERMODINAMICA

TRASFORMAZIONI: \rightarrow SPONTANEE
 \rightarrow NON SPONTANEE

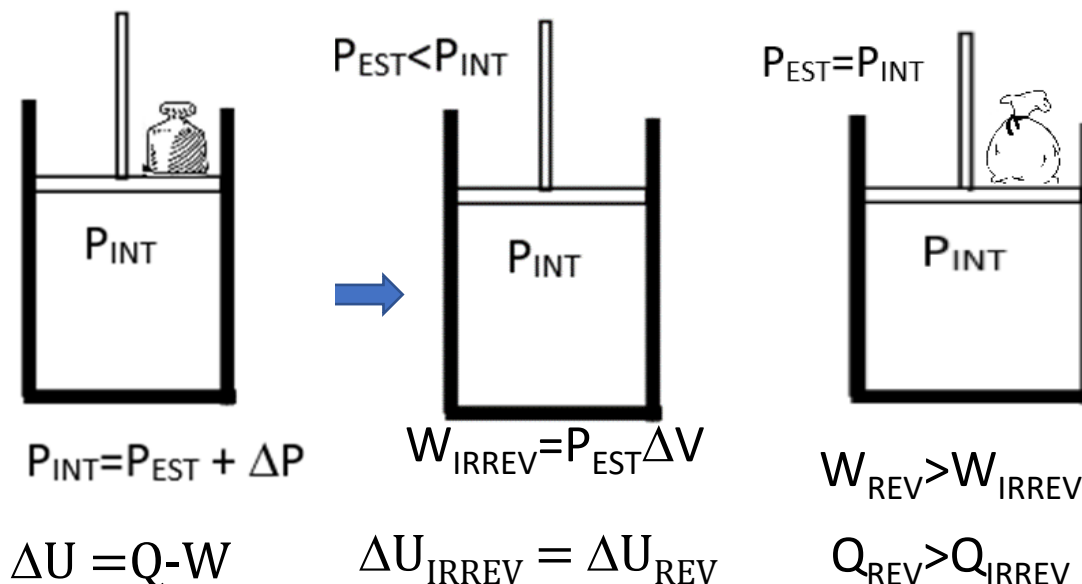
Es.: $H_2O_{(s)} \rightarrow H_2O_{(l)}$ $T = 25^\circ C$

SPONTANEE \rightarrow IRREVERSIBILI
 REVERSIBILI \rightarrow DI EQUILIBRIO

$H_2O_{(s)} \rightleftharpoons H_2O_{(l)}$ $T = 0^\circ C$

IRREVERSIBILE

REVERSIBILE



S ENTROPIA MISURA DEL DISORDINE DEL SISTEMA

$$\Delta S = \frac{Q_{REV}}{T}$$

$$Q_{REV} = \Delta S \cdot T$$

$$\Delta S = \frac{Q_{REV}}{T} \geq \frac{Q_{IRREV}}{T}$$

SISTEMA ISOLATO $Q_{IRREV} = 0$ $\Delta S \geq \frac{Q_{IRREV}}{T} = 0$

$$\Delta S_{TOT} = \Delta S_{SIST} + \Delta S_{AMB} = \Delta S_{UNIV} \geq 0$$



TERZO PRINCIPIO DELLA TERMODINAMICA

$$S = k \cdot \ln \Omega$$

k costante di Boltzmann $k=R/N_A$

Ω = probabilità termodinamica = n° di modi di realizzare il sistema

n° di microstati che corrispondono allo stesso macrostato

Solido cristallino perfetto a 0 K

$$\Omega = 1 \quad S = k \cdot \ln W = k \cdot \ln 1 = 0$$

$$S_{\text{solido}} < S_{\text{liquido}} < S_{\text{gas}}$$

$S^\circ \rightarrow$ Entropia standard

$$\Delta S^\circ_{\text{REAZ}} = \sum_{\text{PROD}} \nu_i S^\circ_i - \sum_{\text{REAG}} \nu_i S^\circ_i \quad \nu_i \text{ coefficiente stechiometrico}$$

$$\Delta S_{\text{TOT}} = \Delta S_{\text{UNIV}} = \Delta S_{\text{SIST}} + \Delta S_{\text{AMB}} \geq 0 \quad \Delta S_{\text{AMB}} \rightarrow \text{difficile da valutare !}$$

- $\Delta S_{\text{UNIV}} > 0$ processo spontaneo, irreversibile
- $\Delta S_{\text{UNIV}} = 0$ processo reversibile, di equilibrio
- $\Delta S_{\text{UNIV}} < 0$ processo non spontaneo, impossibile

L'energia dell'universo è costante, l'entropia dell'universo aumenta sempre

$$\Delta S_{\text{UNIV}} = \Delta S_{\text{SIST}} + \Delta S_{\text{AMB}} \geq 0$$

$$\Delta S_{\text{AMB}} = \frac{Q_{\text{AMB}}}{T} = -\frac{Q_{\text{SIST}}}{T} = -\frac{\Delta H_{\text{SIST}}}{T} \quad P = \text{cost} \quad Q_P = \Delta H$$

$$\Delta S_{\text{UNIV}} = \Delta S_{\text{AMB}} + \Delta S_{\text{SIST}} = -\frac{\Delta H_{\text{SIST}}}{T} + \Delta S_{\text{SIST}} \geq 0$$

$$-T\Delta S_{\text{UNIV}} = \Delta H_{\text{SIST}} - T\Delta S_{\text{SIST}} \leq 0$$

G = H-TS → ENERGIA LIBERA

$$\Delta G_{\text{SIST}} = \Delta H_{\text{SIST}} - T\Delta S_{\text{SIST}} \leq 0 \rightarrow \Delta S_{\text{UNIV}} \geq 0$$

$\Delta G = -W_{\text{UTILE}}$

$$\Delta H - T\Delta S = \Delta G \leq 0$$

$\Delta H < 0 \quad \Delta S > 0 \quad \Delta G < 0 \quad \text{SPONTANEO}$

$\Delta H > 0 \quad \Delta S < 0 \quad \Delta G > 0 \quad \text{NON SPONTANEO}$

$\Delta H > 0 \quad \Delta S > 0 \quad \Delta G ? \quad \text{SPONTANEO AD ALTA T}$

Es.: $\text{H}_2\text{O}_{(s)} \rightarrow \text{H}_2\text{O}_{(l)}$

$\Delta H < 0 \quad \Delta S < 0 \quad \Delta G ? \quad \text{SPONTANEO A BASSA T}$

Es.: $\text{H}_2\text{O}_{(l)} \rightarrow \text{H}_2\text{O}_{(s)}$

$G^\circ_F = H^\circ_F - TS^\circ$ ENERGIA LIBERA STANDARD di FORMAZIONE

G°_F T = 25°C, P = 1 atm

$$\Delta G^\circ_{\text{REAZ}} = \sum_i v_i G^\circ_{F i} - \sum_i v_i G^\circ_{F i} \quad v_i \text{ coefficiente stechiometrico}$$

PRODOTTI REAGENTI

$$\Delta G^\circ_{\text{REAZ}} = \Delta H^\circ_{\text{REAZ}} - T \Delta S^\circ_{\text{REAZ}}$$

$$\Delta H^\circ_{\text{REAZ}} = \sum_i v_i H^\circ_{F i} - \sum_i v_i H^\circ_{F i}$$

PRODOTTI REAGENTI

$$\Delta S^\circ_{\text{REAZ}} = \sum_i v_i S^\circ_i - \sum_i v_i S^\circ_i$$

PRODOTTI REAGENTI

$G = f(T, P)$ G°_F T = 25°C, P = 1 atm

T $G^\circ_F = H^\circ_F - TS^\circ$ $H^\circ_F, S^\circ \sim \text{costanti}$ $G^\circ_F = f(T)$

$$G = H - TS \quad H = E + PV \quad \Rightarrow \quad G = E + PV - TS$$

$$dG = dE + PdV + VdP - TdS - SdT$$

$$E = Q - W \Rightarrow dE = \delta Q - \delta W = TdS - PdV \quad \Rightarrow \quad dE - TdS + PdV = 0$$

$$dG = \underline{dE} + \underline{PdV} + VdP - \underline{TdS} - SdT = VdP - SdT$$

$$T = \text{costante} \quad dG = VdP$$

Gas
ideale

$$V = \frac{RT}{P} \Rightarrow dG = \frac{RT}{P} dP$$

$$\Delta G = G - G^\circ = \int_{G^\circ}^G dG = \int_{P^\circ}^P \frac{RT}{P} dP = RT \ln \frac{P}{P^\circ}$$

$$G = G^\circ + RT \ln \frac{P}{P^\circ} \quad P^\circ = 1,0 \text{ atm} \quad G = G^\circ + RT \ln P$$