

Laws of Thermodynamics

Thermodynamics: (developed in 19th century)

phenomenological theory to describe equilibrium properties of macroscopic systems based on few macroscopically measurable quantities

thermodynamic limit (boundaries unimportant)

state variables / state functions:

describe equilibrium state of TD system uniquely

intensive: homogeneous of degree 0, independent of system size

extensive: homogeneous of degree 1, proportional to system size

intensive state variables serve as *equilibrium parameters*

Laws of Thermodynamics

state variables / state functions:

intensive	extensive
T temperature	S entropy
p pressure	V volume
H magnetic field	M magnetization
E electric field	P dielectric polarization
μ chemical potential	N particle number

conjugate state variable: combine together to an energy

$T S, pV, HM, EP, \mu N$ unit [energy]

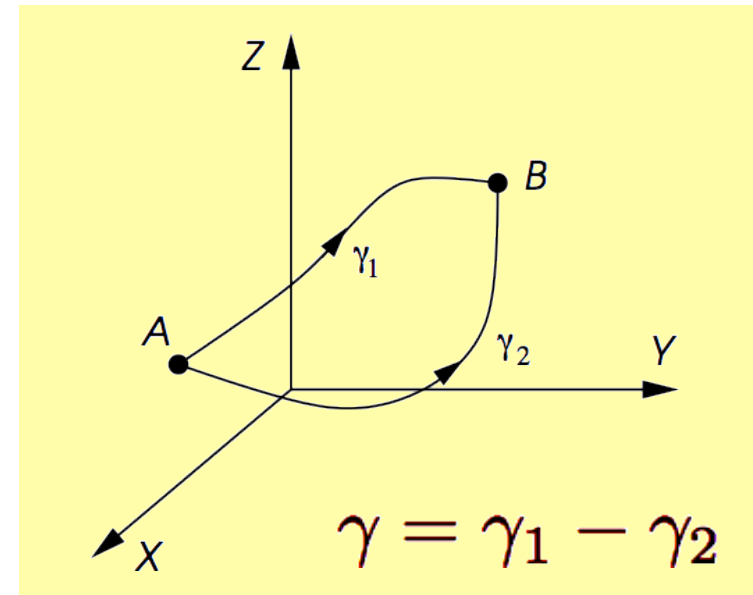
Laws of Thermodynamics

state variable: $Z(X, Y)$

$$\begin{aligned} Z(B) &= Z(A) + \int_{\gamma_1} dZ \\ &= Z(A) + \int_{\gamma_2} dZ \end{aligned}$$



$$\oint_{\gamma} dZ = 0$$



$$dZ = \left(\frac{\partial Z}{\partial X} \right)_Y dX + \left(\frac{\partial Z}{\partial Y} \right)_X dY$$

Z : exact differential



$$\left[\frac{\partial}{\partial Y} \left(\frac{\partial Z}{\partial X} \right)_Y \right]_X = \left[\frac{\partial}{\partial X} \left(\frac{\partial Z}{\partial Y} \right)_X \right]_Y$$

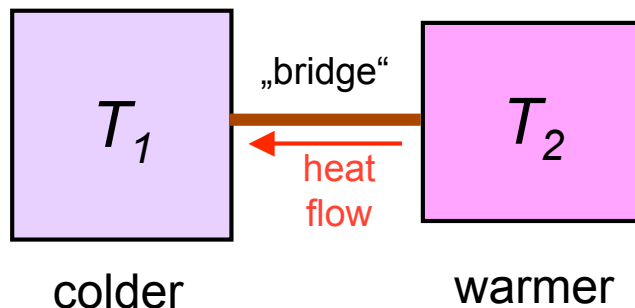
Laws of Thermodynamics

Equilibrium parameters:

intensive state variables can serve as equilibrium parameters

Temperature (existence: 0th law of thermodynamics)

characterizes state of TD systems



$$T_1 < T_2$$

Fick's law

$$\vec{J}_Q = -K \vec{\nabla} T(\vec{r})$$

heat
current

temperature
gradient

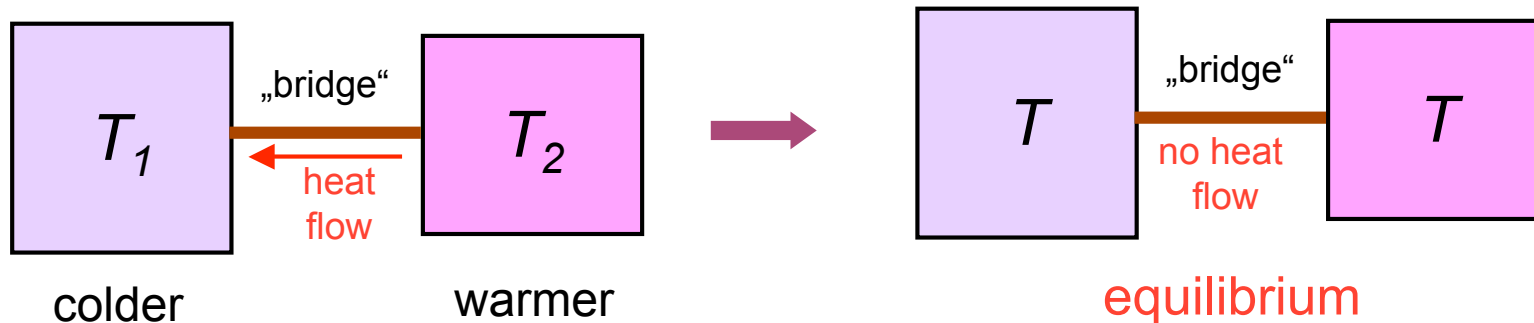
Laws of Thermodynamics

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equilibrium

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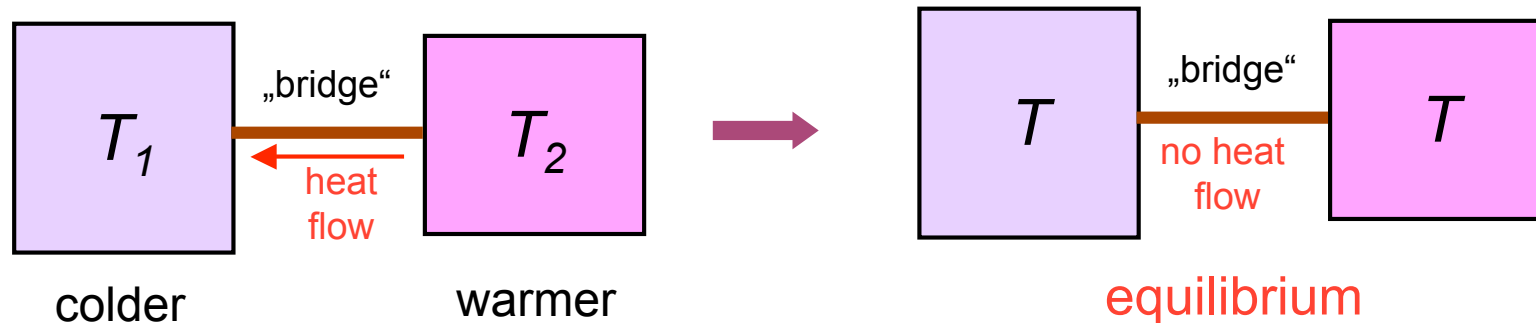
Laws of Thermodynamics

Equilibrium parameters:

intensive state variables can serve as equilibrium parameters

Temperature (existence: 0th law of thermodynamics)

characterizes state of TD systems



other equilibrium parameters:

pressure p
chemical potential μ

equilibrium parameter
constant everywhere
in TD system

Laws of Thermodynamics

Equations of state:

consider TD system described by state variables $\{Z_1, Z_2, \dots, Z_n\}$

subspace of equilibrium states:

$$f(Z_1, Z_2, \dots, Z_n) = 0$$

equation of state (EOS)

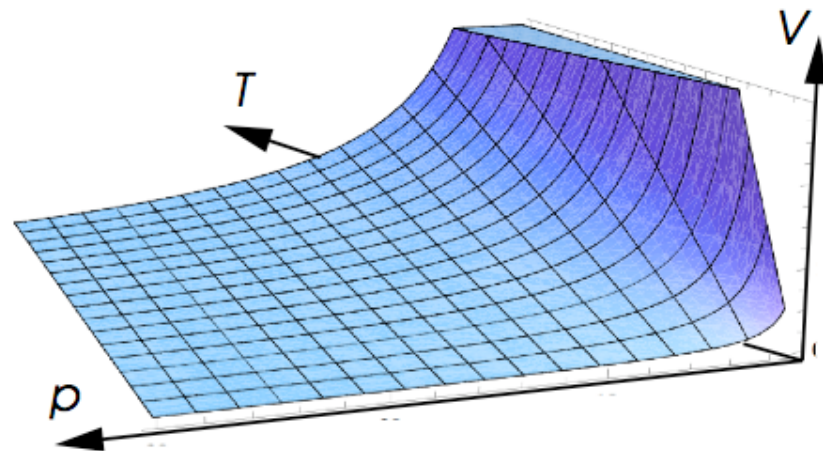
Ideal gas: $\{T, p, V\}$

thermodynamic EOS

$$pV = Nk_B T$$

Boltzmann constant

$$k_B = 1.381 \cdot 10^{-23} JK^{-1}$$



Laws of Thermodynamics

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response functions

reaction of TD system to change
of state variables

isobar thermal
expansion coefficient $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p = \frac{1}{T}$

isothermal
compressibility $\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T = \frac{1}{p}$

Laws of Thermodynamics

1st law of thermodynamics

J.R. Mayer, J.P. Joule & H. von Helmholtz

~1850

„heat is like work a form of energy“

heat

$$\delta Q = C dT$$

specific heat

C_V : constant V

C_p : constant p

work

$$\delta W = F dq$$

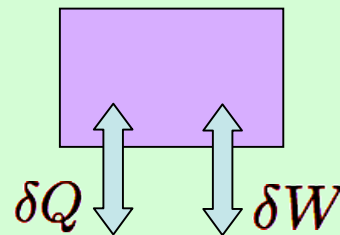
force displacement

$$\delta W = -p dV \quad \text{gas}$$

$$\delta W = H dM \quad \text{paramagnet}$$

internal energy U

$$dU = \delta Q + \delta W$$



isolated TD system

$$\rightarrow dU = 0$$

$$\delta Q = \delta W = 0$$

Laws of Thermodynamics

1st law

internal energy

$$dU = \delta Q + \delta W$$

ideal gas (single atomic): $U = \frac{3}{2}Nk_B T$ (equipartition)
caloric EOS

Specific heat: $\delta Q = dU - \delta W = dU + pdV$

$$= \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + pdV$$

constant V

$$C_V = \left(\frac{\delta Q}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$$

Laws of Thermodynamics

1st law

internal energy

$$dU = \delta Q + \delta W$$

ideal gas (single atomic): $U = \frac{3}{2}Nk_B T$ (equipartition)
caloric EOS

Specific heat: $\delta Q = dU - \delta W = dU + pdV$

$$= \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + pdV$$

constant p

$$C_p = \left(\frac{\delta Q}{dT}\right)_p = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] \left(\frac{\partial V}{\partial T}\right)_p$$

Laws of Thermodynamics

1st law

internal energy

$$dU = \delta Q + \delta W$$

ideal gas (single atomic): $U = \frac{3}{2}Nk_B T$ (equipartition)
caloric EOS

Specific heat:

$$C_p - C_V = \left[\left(\frac{\partial U}{\partial V} \right)_T + p \right] \left(\frac{\partial V}{\partial T} \right)_p = \left[\left(\frac{\partial U}{\partial V} \right)_T + p \right] V \alpha$$

ideal gas: $\begin{cases} \left(\frac{\partial U}{\partial V} \right)_T = 0 \\ \alpha = \frac{1}{T} \end{cases}$ and $pV = Nk_B T \rightarrow$

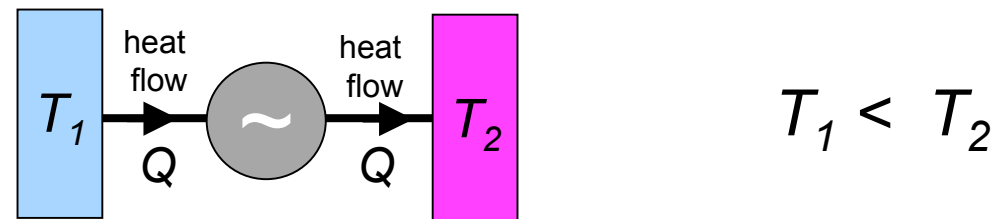
$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{3}{2}Nk_B$$
$$C_p - C_V = Nk_B$$

Laws of Thermodynamics

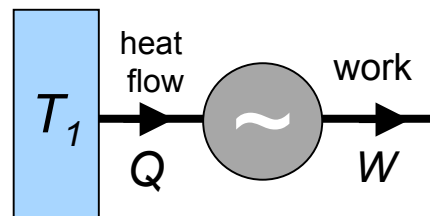
2nd law of thermodynamics

two equivalent formulations

R. Clausius: there is no cyclic process whose only effect is to transfer heat from a reservoir of lower temperature to one with higher temperature



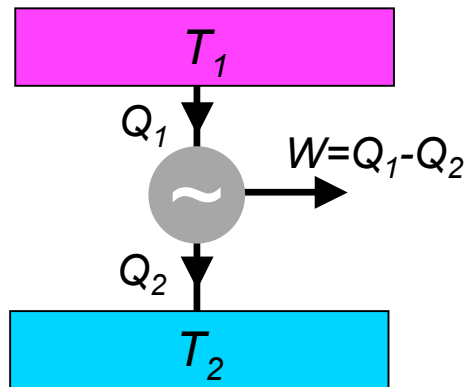
W. Thomson (Lord Kelvin): there is no cyclic process whose effect is to take heat from a reservoir and transform it completely into work;
there is no **perpetuum mobile of the 2nd kind**



Laws of Thermodynamics

2nd law

Carnot engine



reversible Carnot process $\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$

→ definition of absolute temperature T

irreversible process $\frac{Q_1}{Q_2} < \frac{T_1}{T_2}$

entropy as new state variable

$$dS = \frac{\delta Q}{T} \xrightarrow{\text{Clausius' theorem}} dS \geq \frac{\delta Q}{T}$$

$$\oint \frac{\delta Q}{T} \leq 0$$

$$\left\{ \begin{array}{ll} \oint \frac{\delta Q}{T} = 0 & \text{cyclic process reversible} \\ \oint \frac{\delta Q}{T} < 0 & \text{cyclic process irreversible} \end{array} \right.$$

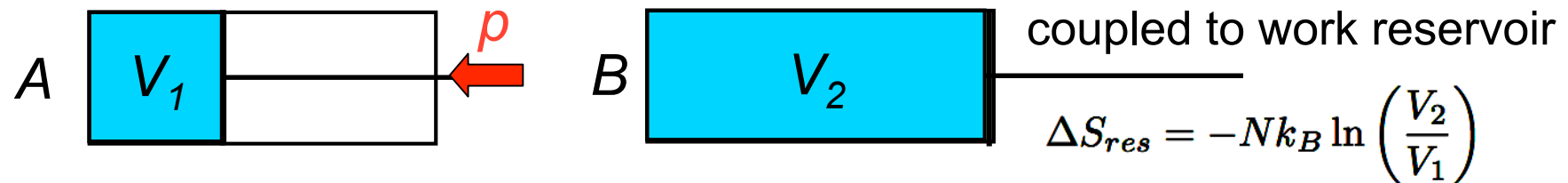
Laws of Thermodynamics

2nd law

entropy

$$dS \geq \frac{\delta Q}{T} \quad \rightarrow \quad \int_A^B \frac{\delta Q}{T} \leq \int_A^B dS = S(B) - S(A)$$

ideal gas: reversible isothermal process $dU=0$ $\delta Q = -\delta W$

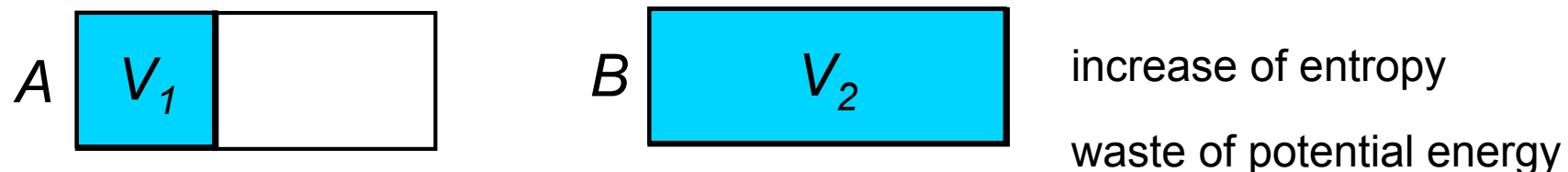


$$\Delta S = \int_A^B \frac{\delta Q}{T} = -\frac{1}{T} \int_{V_1}^{V_2} p dV = Nk_B \ln \left(\frac{V_2}{V_1} \right)$$

$$\Delta S_{tot} = \Delta S + \Delta S_{res} = 0$$

irreversible process $\Delta S_{res} = 0$

$$\Delta S_{tot} = \Delta S + \Delta S_{res} > 0$$



Laws of Thermodynamics

2nd law

application to gas: $TdS = \delta Q = dU - \delta W = dU + pdV$

dS exact differential $S(U, V)$

$$dS = \frac{1}{T}dU + \frac{p}{T}dV = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV$$

- $\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T} \rightarrow T = T(U, V) \rightarrow U = U(T, V)$
caloric EOS
- $\left(\frac{\partial S}{\partial V}\right)_U = \frac{p}{T} \rightarrow p = Tf(T, V)$ thermodynamic EOS

Laws of Thermodynamics

Thermodynamic potentials

natural state variables \rightarrow convenient simple relations

internal energy (gas) $U(S, V)$

$$dU = TdS - pdV \rightarrow \left(\frac{\partial U}{\partial S}\right)_V = T \quad \text{and} \quad \left(\frac{\partial U}{\partial V}\right)_S = -p$$

response functions:

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_V = \left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V}$$

specific heat

$$\left(\frac{\partial^2 U}{\partial V^2}\right)_S = \left(\frac{\partial p}{\partial V}\right)_S = \frac{1}{V\kappa_s}$$

adiabatic compressibility

$dS=0$

Laws of Thermodynamics

Thermodynamic potentials

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$$dU = TdS - pdV \rightarrow \left(\frac{\partial U}{\partial S}\right)_V = T \quad \text{and} \quad \left(\frac{\partial U}{\partial V}\right)_S = -p$$

Maxwell relations:

dU exact differential

$$\left[\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S}\right)_V\right]_S = \left[\frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V}\right)_S\right]_V \rightarrow \left(\frac{\partial T}{\partial V}\right)_S = - \left(\frac{\partial p}{\partial S}\right)_V$$

Laws of Thermodynamics

Thermodynamic potentials

natural state variables \rightarrow convenient simple relations

other variables: $(S, V) \rightarrow (T, V)$ Legendre transformation

Helmholtz free energy (gas) $F(T, V)$

$$F(T, V) = \inf_S \left\{ U - S \left(\frac{\partial U}{\partial S} \right)_V \right\} = \inf_S \{ U - ST \}$$

$$dF = dU - d(ST) = dU - SdT - TdS = -SdT - pdV$$

$$\left. \begin{array}{l} \left(\frac{\partial F}{\partial T} \right)_V = -S \\ \left(\frac{\partial F}{\partial V} \right)_T = -p \end{array} \right\} \xrightarrow{\text{response functions}} \left\{ \begin{array}{l} \left(\frac{\partial^2 F}{\partial T^2} \right)_V = -\frac{C_V}{T} \quad \text{specific heat} \\ \left(\frac{\partial^2 F}{\partial V^2} \right)_T = \frac{1}{V\kappa_T} \quad \text{isothermal compressibility} \end{array} \right.$$

Laws of Thermodynamics

Thermodynamic potentials

natural state variables \rightarrow convenient simple relations

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$$F(T, V) = \inf_S \left\{ U - S \left(\frac{\partial U}{\partial S} \right)_V \right\} = \inf_S \{ U - ST \}$$

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$$\left. \begin{array}{l} \left(\frac{\partial F}{\partial T} \right)_V = -S \\ \left(\frac{\partial F}{\partial V} \right)_T = -p \end{array} \right\} \xrightarrow{\text{Maxwell relation}} \left(\frac{\partial p}{\partial T} \right)_V = \left(\frac{\partial S}{\partial V} \right)_T$$

Laws of Thermodynamics

Thermodynamic potentials

natural state variables \rightarrow convenient simple relations

Enthalpy (gas) $H(S,p)$

$$dH = TdS + Vdp \xrightarrow{\text{Maxwell relation}} \left(\frac{\partial T}{\partial p} \right)_S = \left(\frac{\partial V}{\partial S} \right)_p$$

Gibbs free energy (gas) $G(T,p)$

$$dG = -SdT + Vdp \xrightarrow{\text{Maxwell relation}} \left(\frac{\partial S}{\partial p} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_p$$

Laws of Thermodynamics

Equilibrium condition

entropy: $dS \geq 0$ general
 $dS = 0$ in equilibrium

closed system: $dU=dV=0$

S maximal



U, V fixed variables

fixed variables	potential
T, V	F minimal
T, p	G minimal
S, V	U minimal
S, p	H minimal

Laws of Thermodynamics

3rd law of thermodynamics

Nernst 1905

entropy $S = S(T, q, \dots)$

$$\lim_{T \rightarrow 0} \left(\frac{\partial S}{\partial q} \right)_T = 0 \qquad \lim_{T \rightarrow 0} \left(\frac{\partial S}{\partial T} \right)_q = 0$$

e.g.: $C_V(T = 0) = 0 \qquad \alpha(T = 0) = 0$

$$\lim_{T \rightarrow 0} S(T, q, \dots) = S_0 \quad \text{independent of } T, q, \dots$$

Planck: $S_0 = 0$ only within quantum statistical physics