

Lecture 23: Basic Concepts of Thermodynamics



[Operational definition] Temperature is what you measure with a thermometer.





[Operational definition] Temperature is what you measure with a thermometer.

[Let's go to a hospital] The steps of the measurement are:

- Contact of object and thermometer. What kind of contact?
- Wait for some time. How long shall we wait?
- Read the temperature. How do we quantify?



Contact of object and thermometer. What kind of contact?

– Allowing spontaneous energy transfer, i.e., heat. No particle transfer!

Wait for some time. How long shall we wait?

Relaxation time. Should not be long.

Read the temperature. How do we quantify?

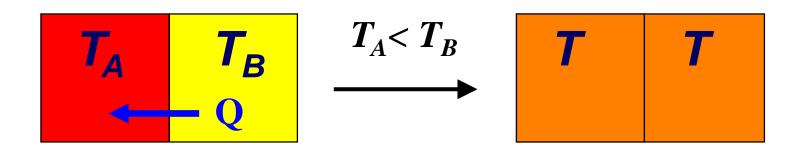
- We need a law, or an equation.

After two objects have been in contact long enough (such that their macroscopic properties no longer change), we say that they are in thermal equilibrium (microscopic properties still change).

The zeroth law of thermodynamics: If two systems are in thermal equilibrium with a third system, then they must be in thermal equilibrium with each other.



[Definition] Temperature is a measure of the tendency of an object to spontaneously give up energy to its surroundings. When two objects are in thermal contact, the one that tends to spontaneously lose energy is at the higher temperature.



Physical properties that change with temperature:

- volume of a liquid
- -length of a solid
- pressure of a gas at constant volume
- volume of a gas at constant pressure
- electric resistance of a conductor

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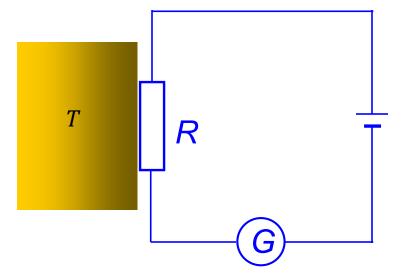
Thermometer I

$$T = \alpha X$$

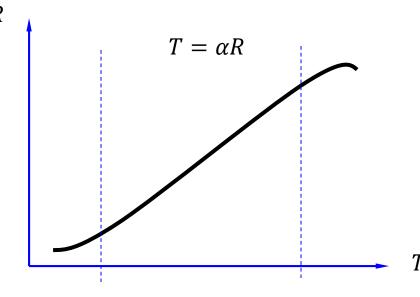
physical quantity

P, V, L, R ...

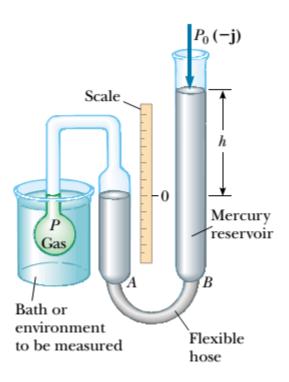
thermoresistance

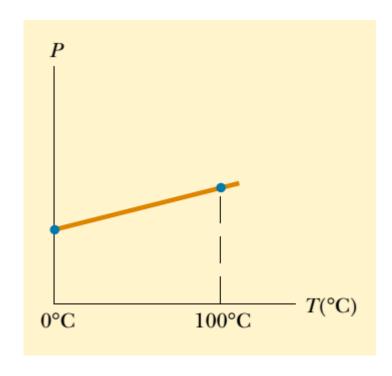


R



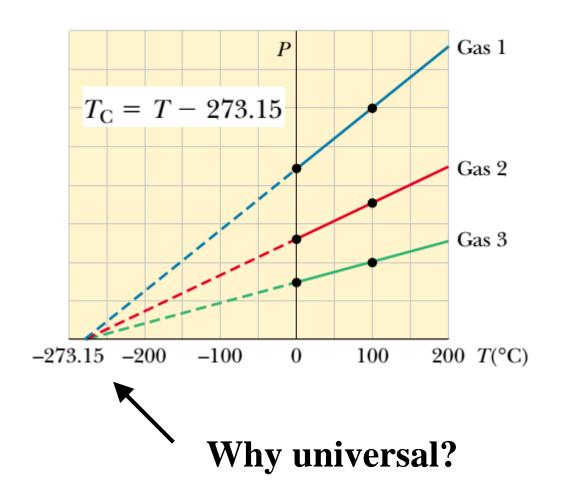
Constant-volume gas thermometer

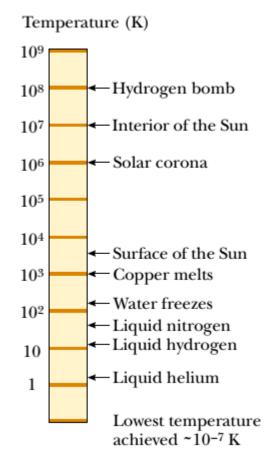






Absolute Zero







The Third Law of Thermodynamics

The third law of thermodynamics: "It is impossible for

any procedure to lead to the isotherm T = 0 in a finite number of steps."

-- Walther Nernst



Temperature Scales

Celsius scale $T_C = T - 273.15$

Fahrenheit scale $T_{\rm F} = \frac{9}{5}T_{\rm C} + 32^{\circ}{\rm F}$

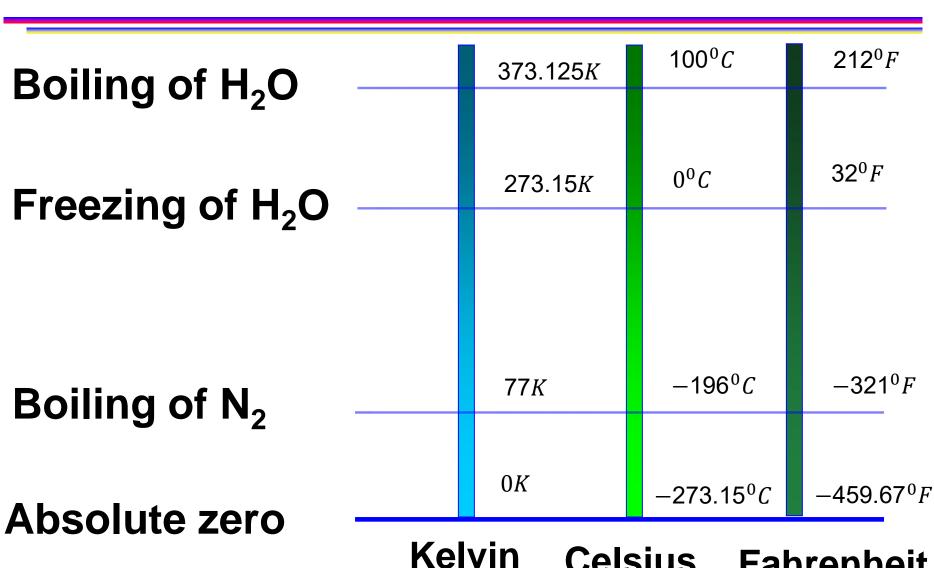
Absolute temperature (Kelvin) scale:

-1/273.16 of the difference between

absolute zero and the temperature of the triple point of water

Water Ice Vapor





Celsius

Fahrenheit



Thermometer III

Thermal Expansion

- Linear expansion

$$T+\Delta T$$

$$\Delta L = a \Delta T + b (\Delta T)^2 + c (\Delta T)^3 + \cdots$$

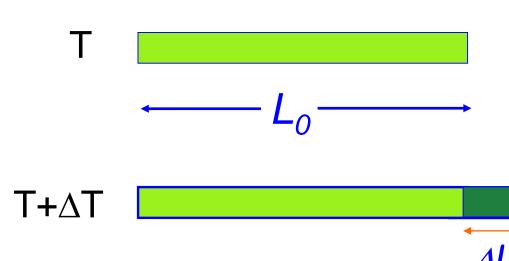


for sufficiently small ΔT



Thermal Expansion

- Linear expansion





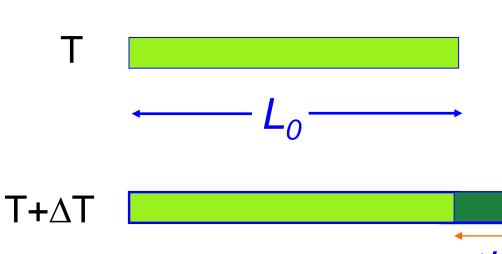
 $\Delta L = a \Delta T$

What should a depend on?



Thermal Expansion

- Linear expansion





$$\Delta L = \alpha L_0 \Delta T$$
, or $L = L_0 (1 + \alpha \Delta T)$

Linear vs Volume Expansion

Thermal Expansion

- Linear expansion $\Delta L = \alpha L_0 \Delta T$
- Volume expansion $\Delta V = \beta V_0 \Delta T$

Are α and β independent coefficients?

Linear vs Volume Expansion

Thermal Expansion

- Linear expansion $\Delta L = \alpha L_0 \Delta T$
- Volume expansion $\Delta V = \beta V_0 \Delta T$

$$L^{3} = (L_{0} + \Delta L)^{3} = [L_{0}(1 + \alpha \Delta T)]^{3}$$
$$= L_{0}^{3} [1 + 3\alpha \Delta T + O(\Delta T)^{2}]$$

$$V = V_0 (1 + \beta \Delta T)$$
 $\rightarrow \beta = 3\alpha$

What should α or β depend on?

- Average distance between molecules
- Size of molecules
- Range of interaction
- •

Material	Average Linear Expansion Coefficient (α) (°C) ⁻¹	Material	Average Volume Expansion Coefficient (β) (°C) ⁻¹
Aluminum	24×10^{-6}	Alcohol, ethyl	1.12×10^{-4}
Brass and bronze	19×10^{-6}	Benzene	1.24×10^{-4}
Copper	17×10^{-6}	Acetone	1.5×10^{-4}
Glass (ordinary)	9×10^{-6}	Glycerin	4.85×10^{-4}
Glass (Pyrex)	3.2×10^{-6}	Mercury	1.82×10^{-4}
Lead	29×10^{-6}	Turpentine	9.0×10^{-4}
Steel	11×10^{-6}	Gasoline	9.6×10^{-4}
Invar (Ni-Fe alloy)	0.9×10^{-6}	Air at 0°C	3.67×10^{-3}
Concrete	12×10^{-6}	Helium	3.665×10^{-3}



A steel railroad track has a length of 30 m when the temperature is 0.0°C. (a) What is its length when the temperature is 40°C?



$$\Delta L = \alpha L_i \Delta T = [11 \times 10^{-6} (^{\circ}\text{C})^{-1}] (30.000 \text{ m}) (40.0^{\circ}\text{C})$$

= 0.013 m

(b) Suppose that the ends of the rail are rigidly clamped at 0.0°C so that expansion is prevented. What is the thermal stress set up in the rail if its temperature is raised to 40.0°C?

Tensile stress =
$$\frac{F}{A} = Y \frac{\Delta L}{L_i}$$

$$= (20 \times 10^{10} \,\mathrm{N/m^2}) \left(\frac{0.013 \,\mathrm{m}}{30.000 \,\mathrm{m}} \right) = 8.7 \times 10^7 \,\mathrm{N/m^2}$$

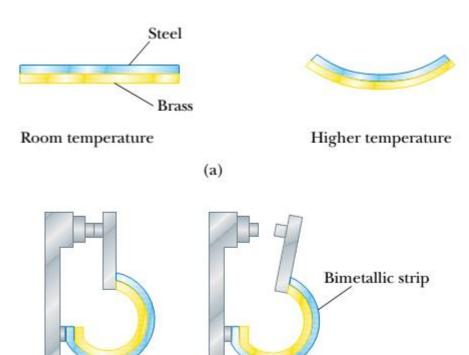


The force of compression in the rail can be as large as 10^5 N! (Assume a cross-sectional area of ~ 10 cm²)





Bimetallic Strip



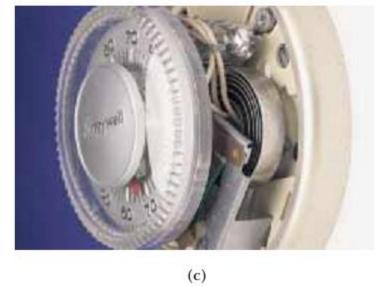
Off

(b)

30°C

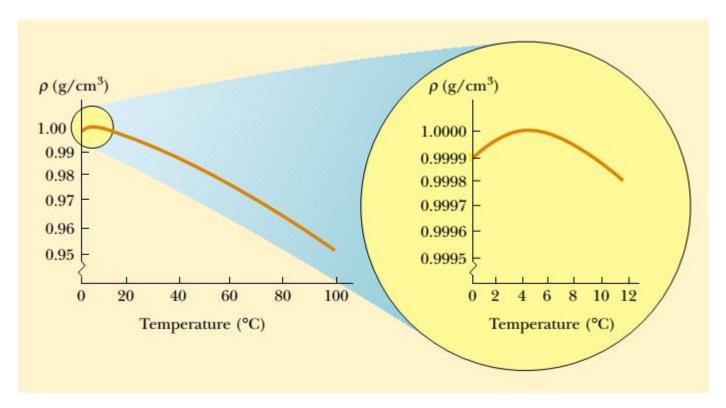
25°C

On





Unusual Behavior of Water



As the water freezes, the ice remains on the surface because ice is less dense than water. The ice continues to build up at the surface, while water near the bottom remains at 4°C.



Equation of state for an ideal gas

$$PV = nRT$$
 (ideal gas law)

$$R = 8.315 \,\mathrm{J/mol \cdot K}$$

$$PV = nRT = \frac{N}{N_A}RT = Nk_BT$$

Experiment observation

Boltzmann's constant
$$k_B = \frac{R}{N_A} = 1.38 \times 10^{-23} J/K$$

Thermal Expansion for Gases

$$PV = nRT$$

$$\ln(V) = \ln(T) + \ln(nR/P)$$

$$\beta = \left(\frac{1}{V}\frac{dV}{dT}\right)_p = \left(\frac{d(\ln V)}{dT}\right)_p = \frac{d(\ln T)}{dT} = \frac{1}{T}.$$

For an ideal gas at 0° C, $\beta = 1 / 273.15 = 0.00366$

What about air? Let's go back and check.

Material	Average Linear Expansion Coefficient (α) (°C) ⁻¹	Material	Average Volume Expansion Coefficient (β) (°C) ⁻¹
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The van der Waals equation of state

At large molecular/atomic spacing—

$$\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = Nk_B T$$

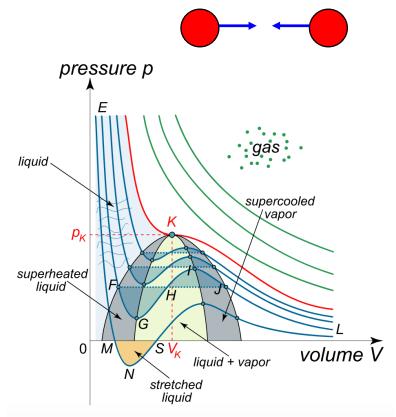
b: volume of a molecule

$$PV = Nk_BT$$

a: due to potential energy

$$T \to 0, V = b$$

$$P \rightarrow P + \frac{aN^2}{V^2}$$





Q&A: Four Real Gases

Why a varies significantly, while b not so much?

	a / [atm (L/mol) ²]	b / (L / mol)
A	0.0341	0.0234
В	1.369	0.0315
С	3.643	0.0427
D	5.507	0.0304

Which is which?

H₂O

 CO_2

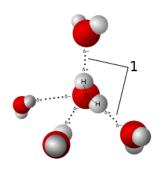


Q&A: Four Real Gases

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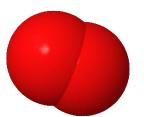
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D	5.507	0.0304

Which is which?



D: **H**₂**O**

A: He



 $C: CO_2$

