Statistical Mechanics and Thermodynamics of Simple Systems

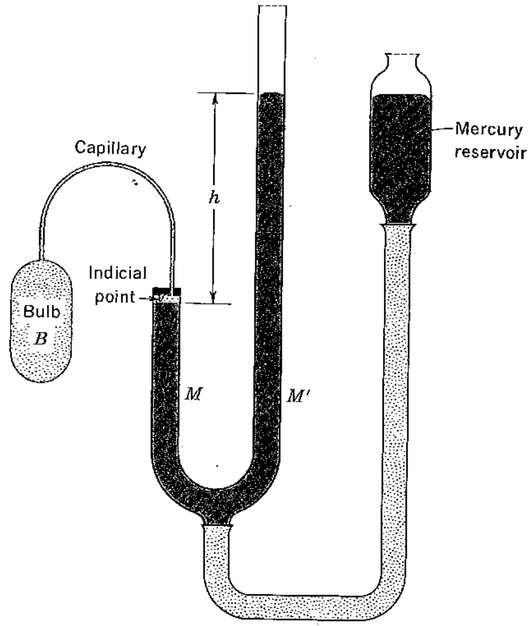
Handout 8

Temperature

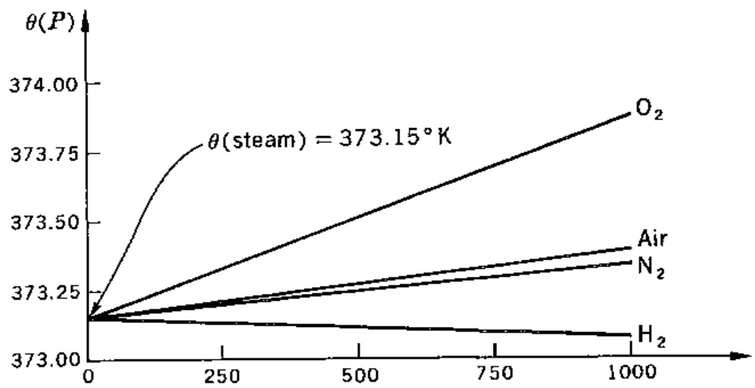
Temperature — a property that determines whether or not a system is in thermal equilibrium with other systems.

Thermometer — a device used to assign a numerical value to temperature through measurement of a physical property.

Constant-volume gas thermometer. The mercury reservoir is raised or lowered to adjust the difference in height h between the two mercury columns M and M' so that the volume of gas in the bulb + capillary is constant.



Pressure variation of the readings of a constant-volume gas thermometer for the temperature of condensing steam, when different gases are used. The readings extrapolate to the same value θ(steam) at low pressure, independent of the gas.



Absolute temperature (perfect gas scale)

$$T(\mathrm{K}) = 273.16 \frac{\lim_{p\to 0}(pV)_T}{\lim_{p\to 0}(pV)_{\mathrm{TP}}},$$

where TP stands for the triple point of water.

Third Law of Thermodynamics

Nernst heat theorem: The entropy change ΔS for a chemical or physical transformation approaches zero at absolute zero,

$$\lim_{T\to 0} \Delta S = 0.$$

Simon's statement of the Third Law: The contribution to the entropy of a system by each aspect which is in internal thermodynamic equilibrium tends to zero at absolute zero.

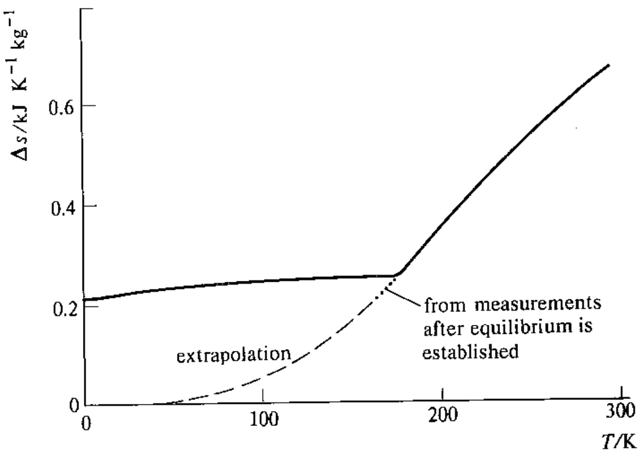
Aspects are separate contributions to the entropy which are calculated independently.

Calculated (statistical) and measured (calorimetric) entropies of gases. Data in the table below are from J. Wilks, *The Third Law of Thermodynamics* (OUP, 1961).

Gas	Temperature (K)	Statistical ($\mathrm{J\,K^{-1}mol^{-1}}$)	Calorimetric ($\mathrm{J\,K^{-1}mol^{-1}}$)
Ar	$87.3^\dagger$	129.7	129.6
O_2	$90.2^\dagger$	170.9	170.9
N_2	$77.3^\dagger$	153.0	153.4
Cl_2	$239.1^\dagger$	216.5	216.6
HCl	$188.0^\dagger$	174.1	173.5
HD	298.1	144.3	144.7
CH_4	$111.6^\dagger$	153.8	153.4
C_2H_4	$169.4^\dagger$	198.9	198.9

† boiling point

Residual entropy due to frozen-in disorder



The diagram shows data for the entropy of supercooled glycerol which freezes just below 300 K. The residual entropy at low temperature (compared with the extrapolated data for glycerol in equilibrium) is due to frozen-in configurational disorder. Figure reproduced from C.J. Adkins, *Equilibrium Thermodynamics* (3rd edition, CUP, 1983).

Unattainability statement of the Third Law: It is impossible to cool any substance to absolute zero in a finite number of processes.

ATB
Michaelmas 2011