

9/26 Lecture outline

- Equation of state: $f(P, V, T) = 0$. Observed fact: at low densities, all fluids have approximately the same equation of state: $PV - n\phi(T) = 0$. Function $\phi(T)$ depends on definition of T . Sensible to take $\phi(T) = aT + b$. All substances have same a and b . Could define T such that $a = 1$ and $b = 0$. Instead, we use Kelvin, $\phi(T) = RT_K$, where $R = 8.3143 \times 10^3 J/(kmole)(degK)$, or Celsius/Centigrade, with $T_C = T_K - 273.15$.

- So at low densities, all fluids have equation of state given approximately by the *ideal gas law* (with T in Kelvin)

$$PV = nRT.$$

- Official SI definition of temperature: Fix constant $a = R$ above by a choice of a reference temperature: triple point of water occurs at a unique temperature, which SI defines to be $T_3 \equiv 273.16K$. (Pressure $P_3 = 0.00602atm$.)

- More general equation of state, $f(P, V, T) = 0$ (for equilibrium). Can solve for $P = P(V, T)$, or $T = T(P, V)$, or $V = V(T, P)$.

- Some math:

$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV.$$

Divide by dP , keeping T constant:

$$1 = \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T.$$

Divide by dT , keeping P constant

$$0 = \left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P.$$

Follows that

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1.$$

- Work done by system $\not{d}W = pdV$. Integrate $\Delta W = \int_{path} pdV$. The slash or bar in $\not{d}W$ is because this is *not* an *exact differential*. What this means, is that ΔW depends on the path, not just the endpoints. Illustrations.

- So $\Delta W \neq W_f - W_i$. Doesn't make sense to discuss W_i and W_f . Work is not a *state variable*.

- Observe: for adiabatic process, then ΔW does depend just on the endpoints. (Special case of first law.)

- Heat transfer. δQ , also not exact. $\Delta Q = \int_{path} \delta Q$ also depends on path. $\Delta Q \neq Q_f - Q_i$. Doesn't make sense to discuss Q_i and Q_f , heat is not a state variable.
- Isochoric process, $dV = 0$, then $\Delta W = 0$, no work done. Observe: for isochoric process, ΔQ does depend just on endpoints. (Special case of first law.)
- First law of thermodynamics: change in internal energy of a system:

$$dU = \delta Q - \delta W,$$

where U is a **state variable**. For system in equilibrium, $U = U(T, V)$, or write as $U = U(P, V)$. Depends only on state of system (which is on the equation of state surface $f(P, V, T) = 0$ for equilibrium).

- For ideal gas, $U = U(T)$, independent of volume. Picture free expansion from V_1 to V_2 , in adiabatically isolated system. No work or heat transfer, so $U_1 = U_2$. Observe that, for dilute enough systems, $T_1 \approx T_2$. We'll later understand the connection between this and the ideal gas law (once we get to the 2nd law of thermo).