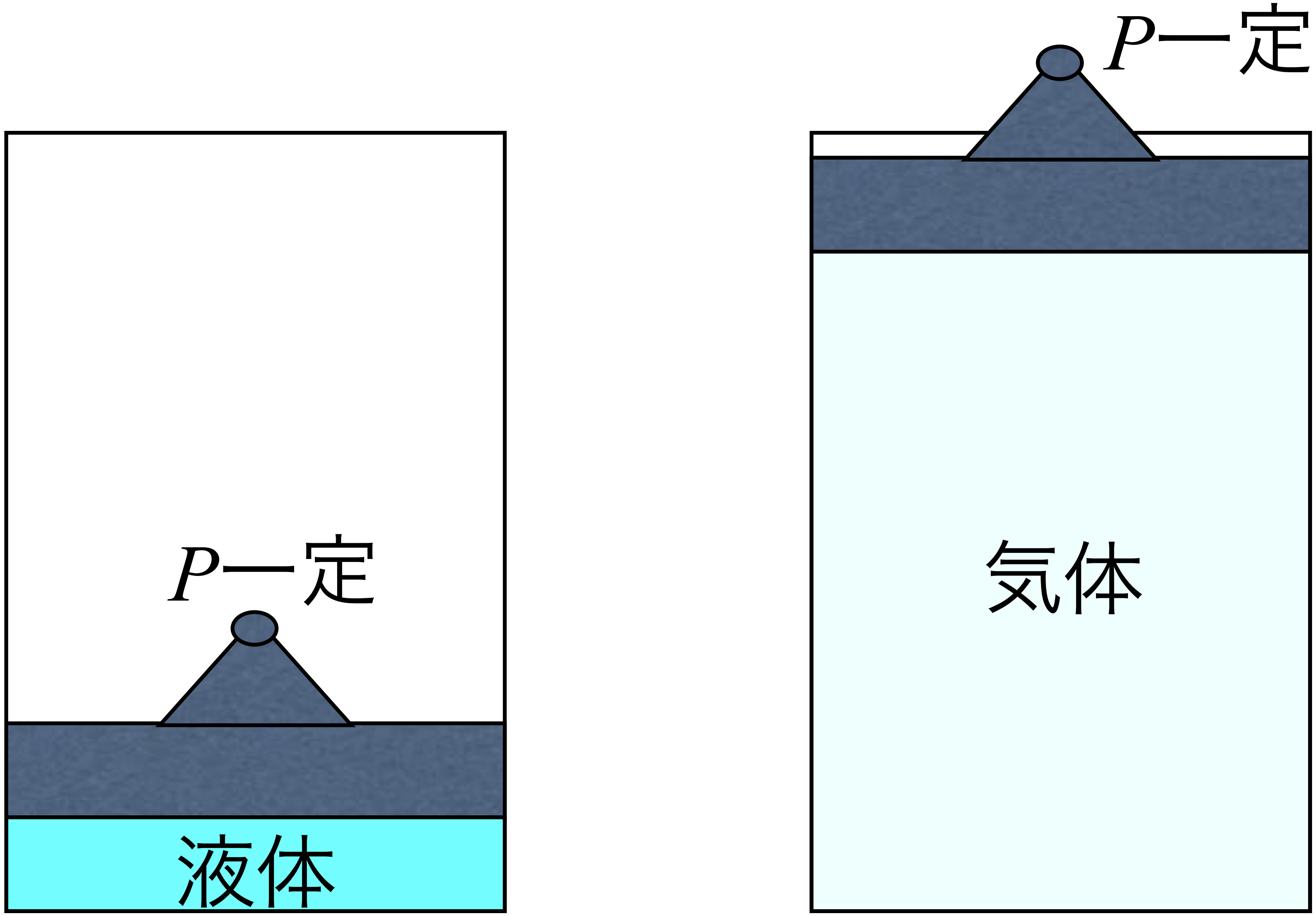
相平衡・
クラウジウス・クラペイロンの式

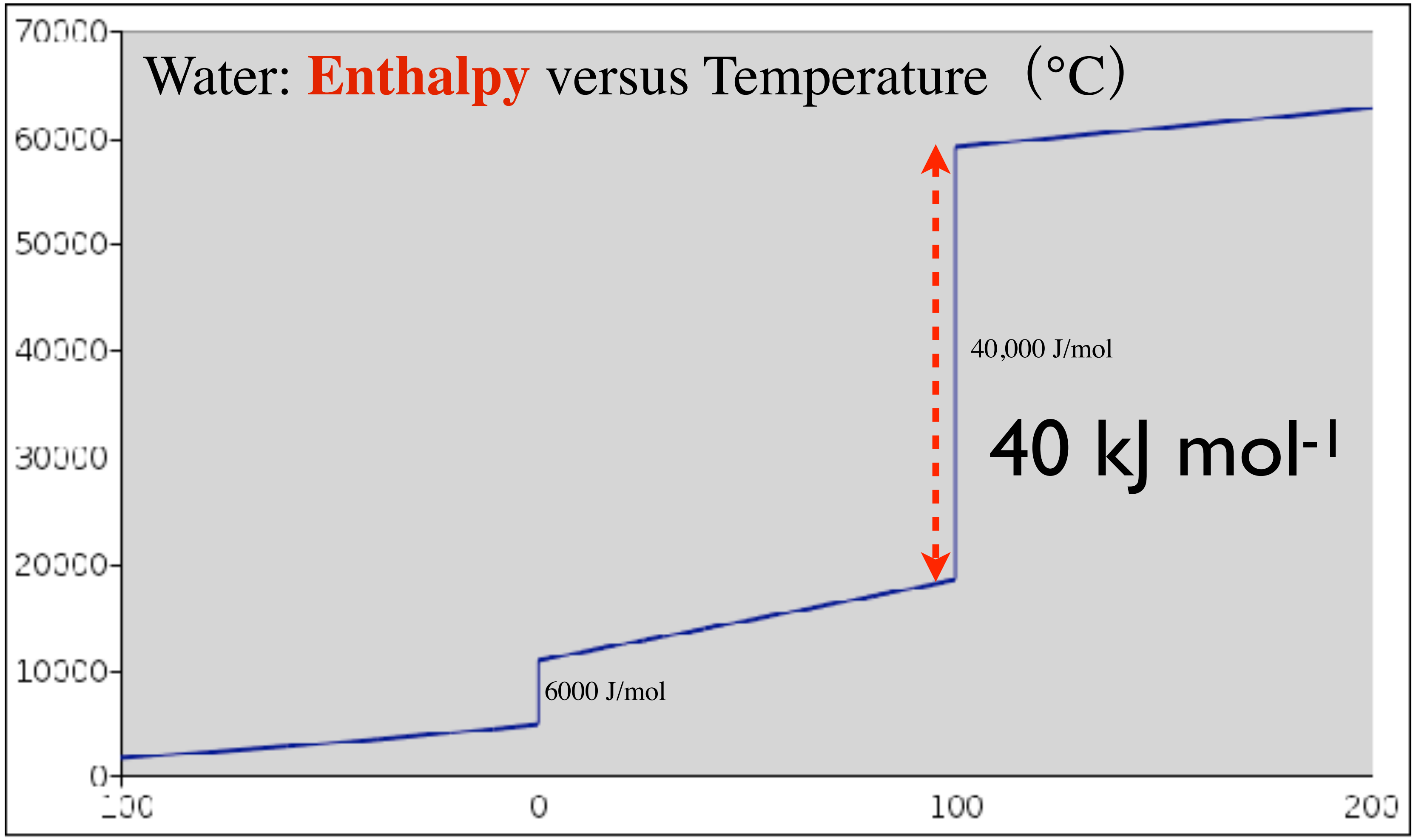
蒸発熱とエンタルピー変化



$$dH = TdS + VdP$$

$$(dH)_P = TdS = dQ$$

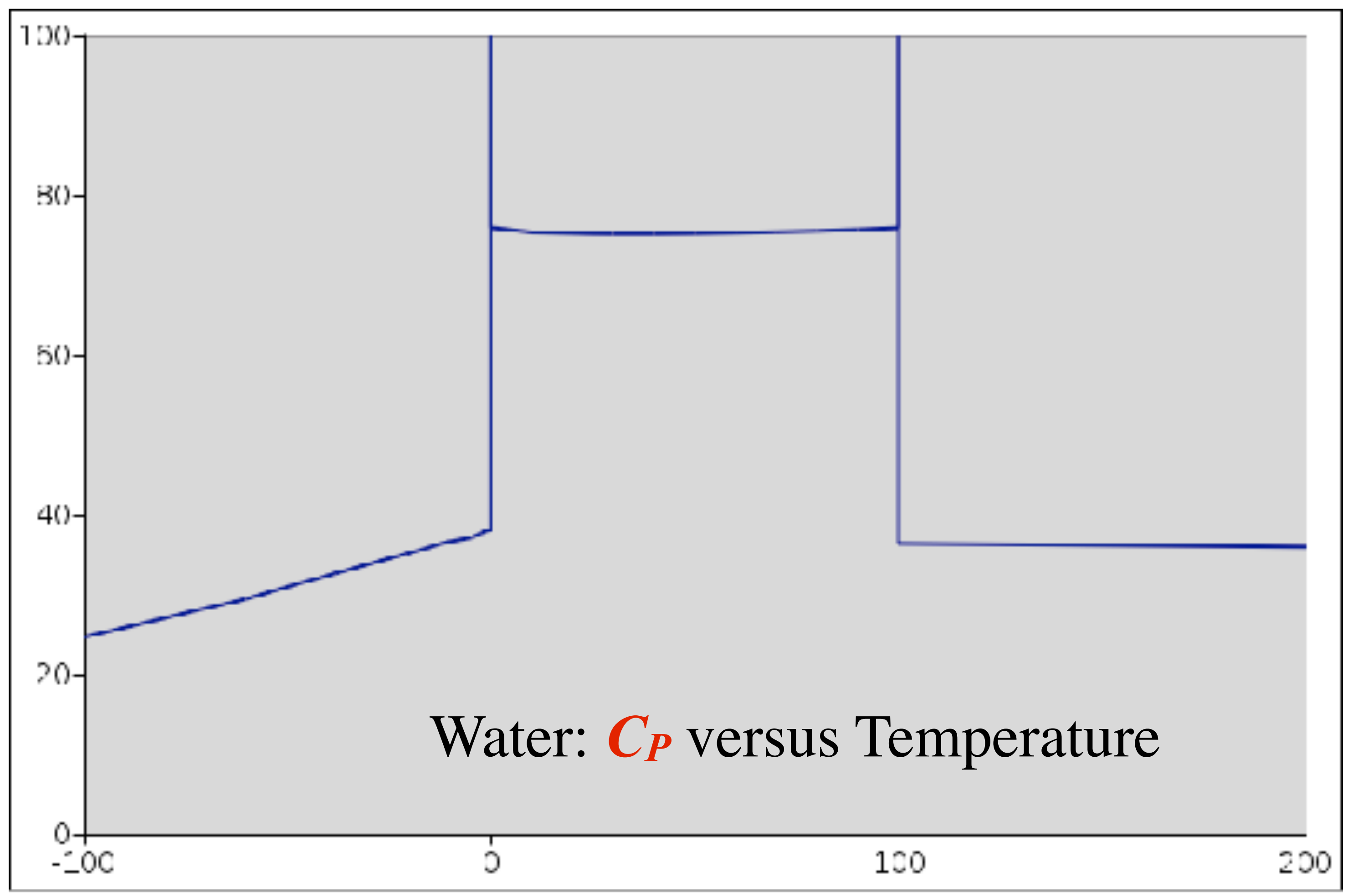
$H_g - H_l$：蒸発熱（蒸発潜熱）



Water: Enthalpy versus Temperature（°C）
70000
60000
50000
40000
30000
20000
10000
0
-100
0
100
200
40,000 J/mol
40 kJ mol-1
6000 J/mol

微分値

定圧熱容量



Water: C_P versus Temperature
100
80
60
40
20
0
-100
0
100
200

水1molが蒸発するときの仕事？

↓水の密度から水の体積

$$\Delta W = -P\Delta V = -P(V_g - V_l) = -RT + 1.013 \times 10^5 \frac{18}{0.96} 10^{-6}$$

$$= -8.314 \times 373 + 1.013 \times 10^5 \frac{18}{0.96} 10^{-6} = -3099\mathrm{J}$$

圧一定なので

$$\Delta H = \Delta Q = 40 \text{ kJ}$$

$$\Delta S = \frac{\Delta Q}{T} = \frac{40000}{373} = 107 \text{ J K}^{-1}$$

$$\Delta U = \Delta Q + \Delta W = 40000 - 3099 = 36901 \text{ J}$$

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

Clapeyron equation　クラペイロンの式

$$\mu_g(T,P) = \mu_l(T,P)$$

$$\mu_g(T+\mathrm{d}T, P+\mathrm{d}P) = \mu_l(T+\mathrm{d}T, P+\mathrm{d}P)$$

$$\mu_g(T,P) + \left(\frac{\partial \mu_g}{\partial T}\right)_P dT + \left(\frac{\partial \mu_g}{\partial P}\right)_T dP = \mu_l(T,P) + \left(\frac{\partial \mu_l}{\partial T}\right)_P dT + \left(\frac{\partial \mu_l}{\partial P}\right)_T dP$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S, \left(\frac{\partial (G/n)}{\partial T}\right)_P = \left(\frac{\partial \mu}{\partial T}\right)_P = -\bar{S}$$

$$\left(\frac{\partial G}{\partial P}\right)_P = V, \left(\frac{\partial (G/n)}{\partial P}\right)_T = \left(\frac{\partial \mu}{\partial T}\right)_P = \bar{V}$$

$$-\bar{S}_g dT + \bar{V}_g \mathrm{d}P = -\bar{S}_l dT + \bar{V}_l \mathrm{d}P$$

$$(\bar{V}_g - \bar{V}_l)\mathrm{d}P = (\bar{S}_g - \bar{S}_l) dT$$

$$\boxed{\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta_{\mathrm{vap}}\bar{S}}{\Delta_{\mathrm{vap}}\bar{V}} = \frac{\Delta_{\mathrm{vap}}\bar{H}}{T\Delta_{\mathrm{vap}}\bar{V}}}$$

Clapeyron equation

$$\Delta_{\mathrm{vap}}\bar{V} = \bar{V}_g - \bar{V}_l \simeq \bar{V}_g = \frac{RT}{P}$$

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{P\Delta_{\mathrm{vap}}\bar{H}}{RT^2}$$

$$\frac{\mathrm{d}P}{P} = \frac{\Delta_{\mathrm{vap}}\bar{H}}{R}\frac{\mathrm{d}T}{T^2}$$

$$\int_{P_1}^{P_2} P^{-1}\mathrm{d}P = \frac{\Delta_{\mathrm{vap}}\bar{H}}{R}\int_{T_1}^{T_2} T^{-2}\mathrm{d}T$$

$$\ln P_2 - \ln R_1 = \frac{\Delta_{\mathrm{vap}}\bar{H}}{R}\left(-\frac{1}{T_2} + \frac{1}{T_1}\right)$$

$$\boxed{\ln\frac{P_2}{P_1} = \frac{\Delta_{\mathrm{vap}}\bar{H}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

Clausius-Clapeyron equation
クラウジウス・クラペイロンの式

蒸気圧と沸点

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H_v}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

富士山の山頂でお湯は何度で沸く？

-1 hPa / 10 m

P_1: 0 m 1013 hPa

富士山頂 3776 m

T_1=373 K

ΔH_v = 40 kJ mol[-1]

P_2: 1013 - 378=635 hPa

$$\ln \frac{635*100}{1013*100} = -\frac{40*1000}{8.314}\left(\frac{1}{T_2} - \frac{1}{373}\right)$$

$$\frac{-0.467*8.314}{-40000} + \frac{1}{373} = \frac{1}{T_2}$$

$$T_2 = 360\text{K} = 87\ ^\circ\text{C}$$

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H_v}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

エベレストの頂上(8848 m)では？

P_1: 0 m 1013 hPa　　　T_1=373 K

P_2: 300 hPa （実測値）　　　ΔH_v = 40 kJ mol^{-1}

$$\ln \frac{300}{1013} = -\frac{40000}{8.314}\left(\frac{1}{T_2} - \frac{1}{373}\right)$$

$$T_2 = 341 \text{ K} = 68 \text{ ℃}$$

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H_v}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

1 atm ベンゼンの沸点 80°C

(P_1, T_1)

80+273= 353 K

ΔH_v = 31 kJ mol^{-1}

P_2 atm ベンゼンの沸点 25°C

(P_2, T_2)

25+273= 298 K

$$\ln \frac{P_2}{1} = -\frac{31000}{8.31}\left(\frac{1}{298} - \frac{1}{353}\right) = -1.950$$

$$\exp(\ln P_2) = P_2 = \exp(-1.950) = 0.14(2) \text{ atom}$$

圧力鍋では沸点は？