Fluides de travail pour la production de froid

Aspects calorimétriques

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Colloque SFGP-SFT du groupe de travail Thermodynamique sur :
Les fluides de travail pour la production de froid
Mercredi 15 mars 2017

UNIVERSITÉ Clermont Auvergne

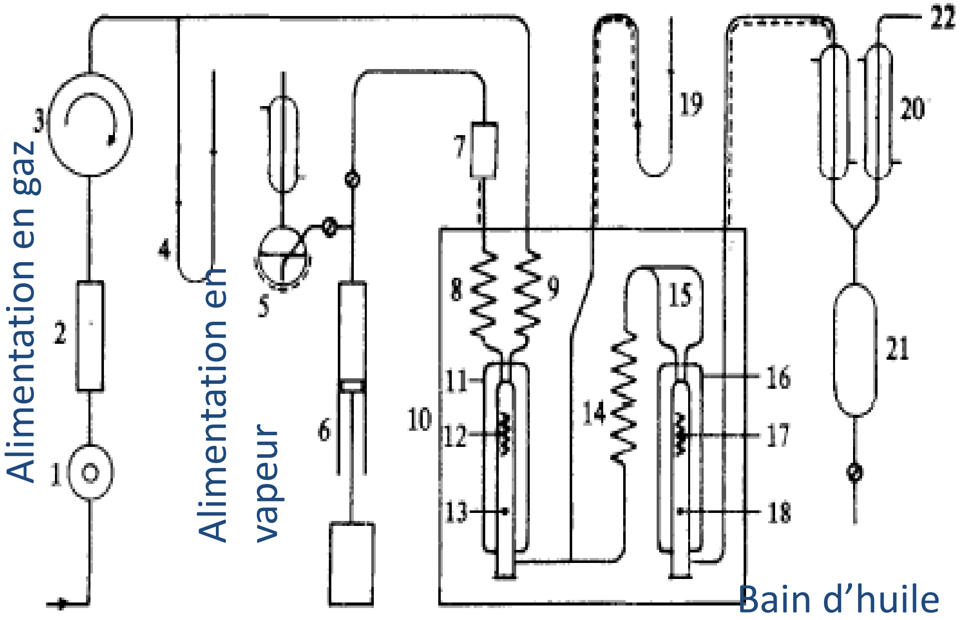
Institut de Chimie de Clermont-Ferrand

Calorimétrie de mélange à basse température

Auteur	T / K	Pression	Fluides
Wormald Wormald, C. J. *J. Chem. Thermodyn.* **9,** 901(1977) Elliott, K. and Wormald, C. J. *J. Chem. Thermodyn.* **8,** 881-893 (1976)	200 - 400	P_{atm} – 10 MPa	gaz-gaz
Zollweg Gopal, P.; Zollweg, J. A. and Streett, W. B. *Rev. Sci. Instrum.* **60,** 2720(1989)	77 - 300	P_{atm} – 15 MPa	Liq-Liq Liq-gaz Gaz-gaz
Siddiqi Siddiqi, M. A. and Lucas, K. J. *J. Chem. Thermodyn.* **14,** 1183(1982)	270-475	P_{atm} – 40 MPa	Liq-Liq Liq-gaz Gaz-gaz
Christensen Christensen, J. J.; Izatt, R. M.; Eatough, D. J. and Hansen, L. D. *J. Chem. Thermodyn.* **10,** 25(1978) Ott, J. B.; Stouffer, C. E.; Cornett G.V.; Woodfield, B. F.; Wirthlin, R. C.; Christensen, J. J. and Deiters, U. K. *J. Chem. Thermodyn.* **18,** 1-12 (1986)	270 - 343	P_{atm} – 40 MPa	Liq-Liq Liq-gaz
Poledníček M. Polednicek, V. Majer, V. Hynek, J. JoseReview Of Scientific Instruments 76, 074102 2005	243 – 348	P_{atm} – 14 MPa	Liq-Liq Liq-gaz

Calorimétre Wormald / Montage

C. J. Wormald J. Chem.T hermodynamics 1977,9, 901-910



Calorimètre isotherme à écoulement

Montage différentiel

T : 363 – 413 K (bain thermostaté)
P : atmosphérique
Débit : 1 – 2. 5mmol/s
Mélange: gaz - gaz

gas
1 flow controller 1
2 dryer calcium chloride
3 oil-filled rotary gasmeter
4 manometer
5 degassing by boiling in flask 5.

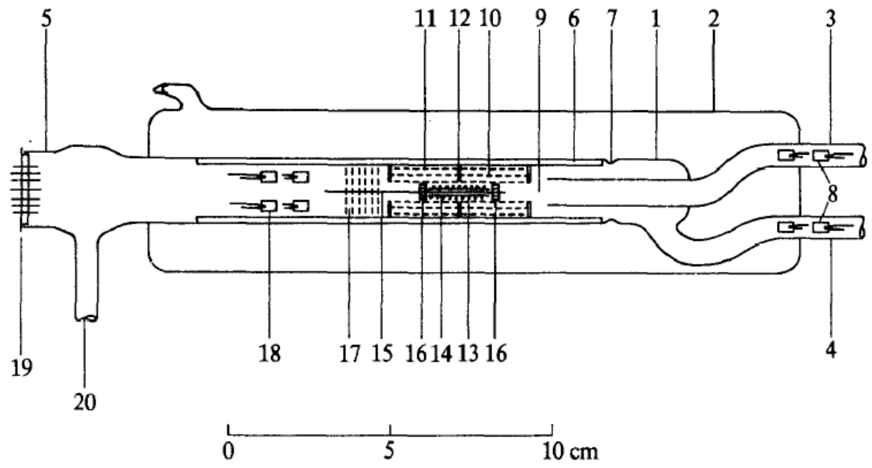
Vapor
6 screw-driven speed piston pump
7 boiler
8-9 heat-exchange coils
10 oil bath 10 controlled to0.002 K

Mixing cell
11-16 mixing point
12-17 heater
13-18 temperature sensors

14 heat-exchange coil
19 mercury manometer 19
20 condenser
21 collecting vessel

Calorimétre Wormald / Cellule de mélange

C. J. Wormald J. Chem.T hermodynamics 1977,9, 901-910



Compensation de puissance
Mesure : Effets endothermiques

Temperature entering gases : thermocouples	8
Mixing point :	9
Heater :	13
Temperature gas mixture :	18

Calorimétre Wormald / exemple d'appliacation

C. J. Wormald J. Chem.T hermodynamics 1977,9, 901-910

Méthane + Benzène (vapeur)

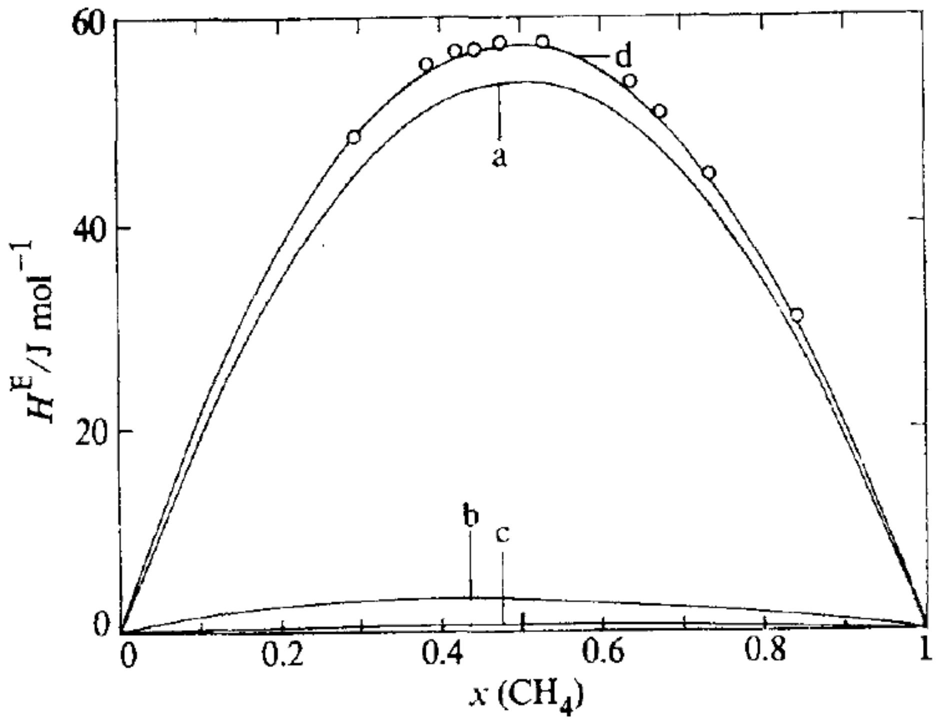
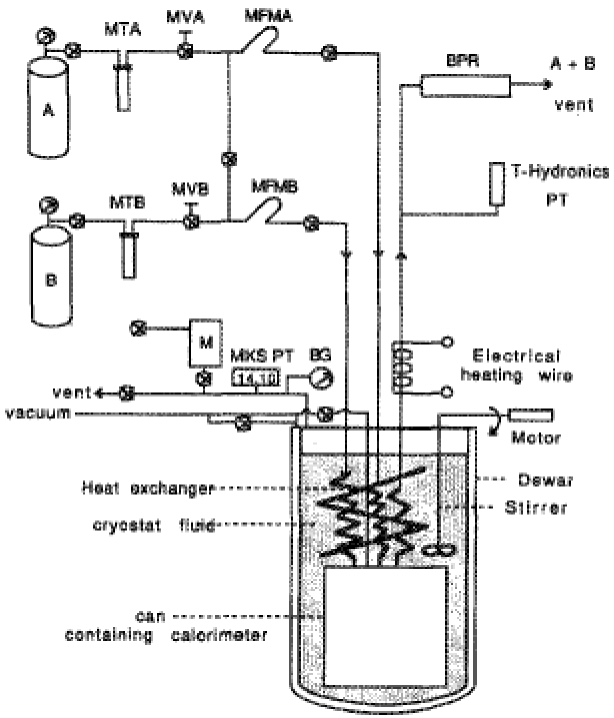


FIGURE 3. Comparison of the experimental results on methane + benzene at 373.15 K with equation (4). Curves a, b, and c are the first, second, and third terms of equation (6). Curve d is the sum of the three terms. ○, This work.

Calorimétre Zollweg / Montage

J.C.G. Calado, P. Palj, J. A. Zollweg, W. R. Thompson Canadian Journal of Chemistry 66(4):626-627 · February 1988
P. Gopal, J.A. Zollweg, W.B. Streett. Rev . Sci. Instrum. 1989 , 60, 2720–2723



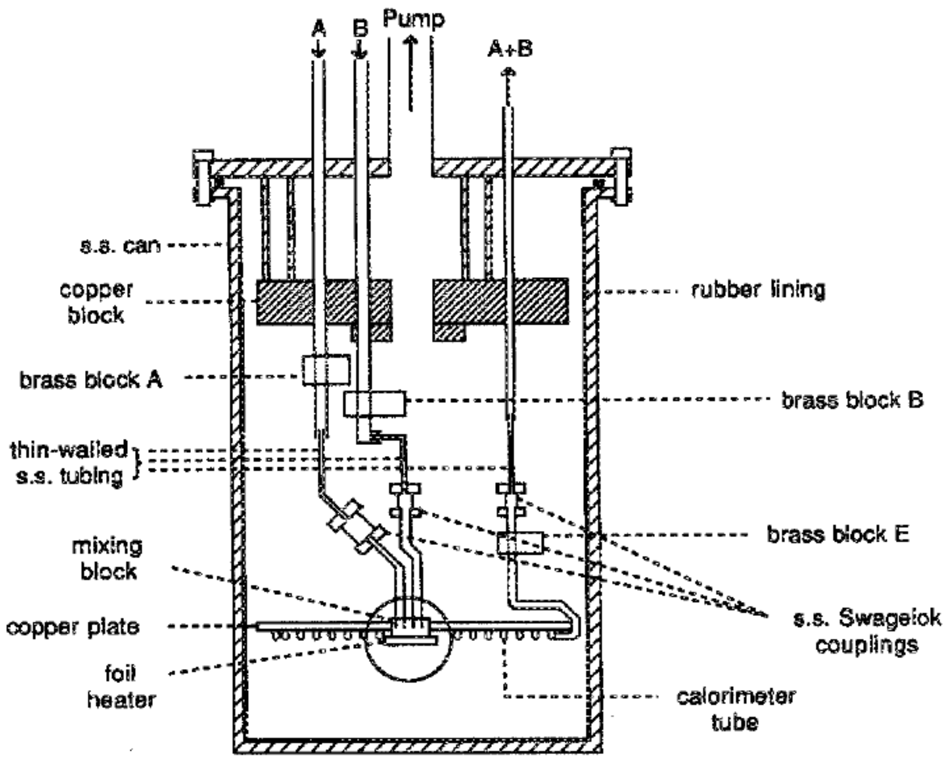
MT moisture trap
MV metering valve
MFM mass flow meter
PT pressure transducer
BPR back pressure regulator
BG bourdon gauge
M manostat

Calorimètre isotherme à écoulement
Débit : 4 – 10 mmol/s

T : 77K -300K (bain thermostaté)
P : < 2 MPa

Calorimétre Zollweg / Cellule

J.C.G. Calado, P. Palj, J. A. Zollweg, W. R. Thompson Canadian Journal of Chemistry 66(4):626-627 · February 1988
P. Gopal, J.A. Zollweg, W.B. Streett. Rev . Sci. Instrum. 1989 , 60, 2720–2723



Compensation de puissance
Mesure : Effets endothermiques

Calorimétre Zollweg / Exemple d'application

J.C.G. Calado, P. Palj, J. A. Zollweg, W. R. Thompson Canadian Journal of Chemistry 66(4):626-627 · February 1988
P. Gopal, J.A. Zollweg, W.B. Streett. Rev . Sci. Instrum. 1989 , 60, 2720–2723

Azote + éthane

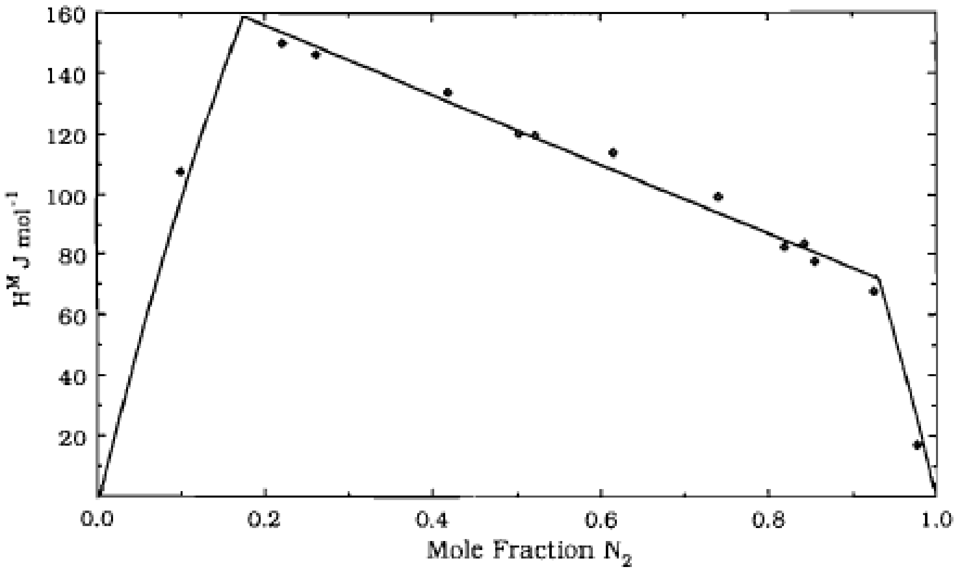


FIG. 1. Heat-of-mixing versus mole fraction for N_2/C_2H_6 at 92.3 K, 0.6309 MPa. The solid line gives a continuous representation of H^M vs. composition.

Calorimétre Siddiqi / Montage

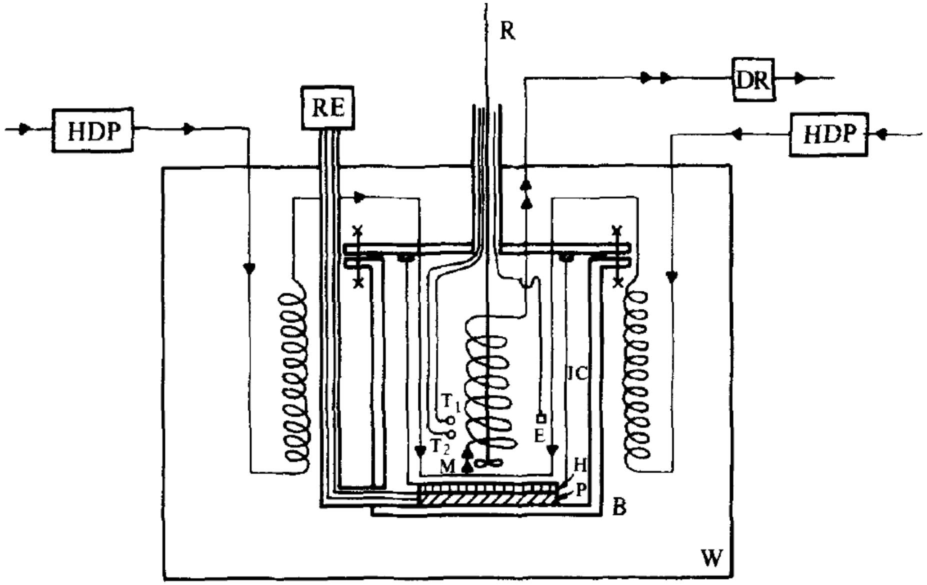


FIGURE 1. Block diagram of the isothermal flow calorimeter. HDP, high-pressure pumps; B, calorimeter vessel; T_1, monitor thermistor; T_2, control thermistor; W, constant-temperature bath; IC, inner cell; H, control heater; M, mixing coil; E, calibration heater; DR, pressure regulator; R, glass stirrer; RE, isothermal control electronics; P, Peltier cooler; EC, equilibrating coils.

Calorimètre isotherme à écoulement
T : 243 – 263 K (bain thermostaté)
P : < 42 Pa
Débit : 0.1 – 10 mL/min
Compensation de puissance
Mesure : Effets endothermiques et Exothermiques
Sensibilité : 5 – 500 mW

Calorimètre Christensen BYU / Montage

J.J. Christensen, P.R. Brown and R.M.Izatt *Thermochimica Acta*, 99 (1986), 159-168

Calorimètre isotherme à écoulement
T : bain thermostaté (ou   773 K)
P : < 40 MPa
Débit : 0.1 – 1 mL/min

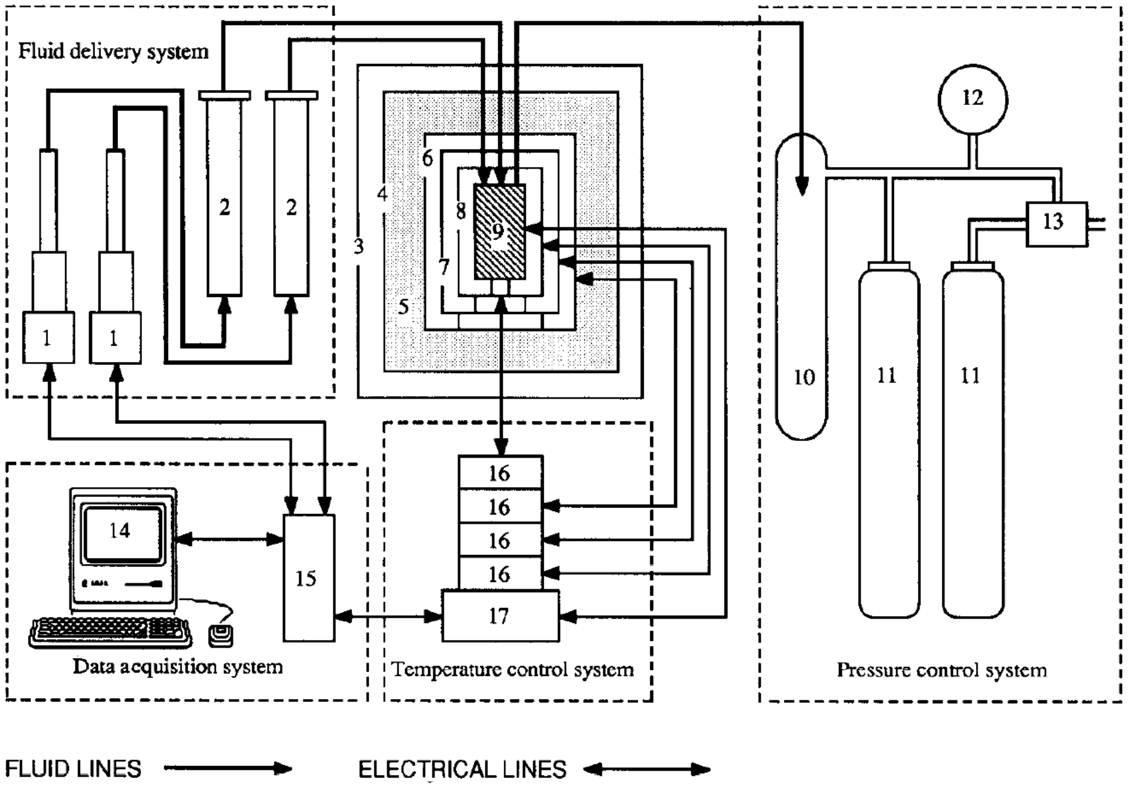
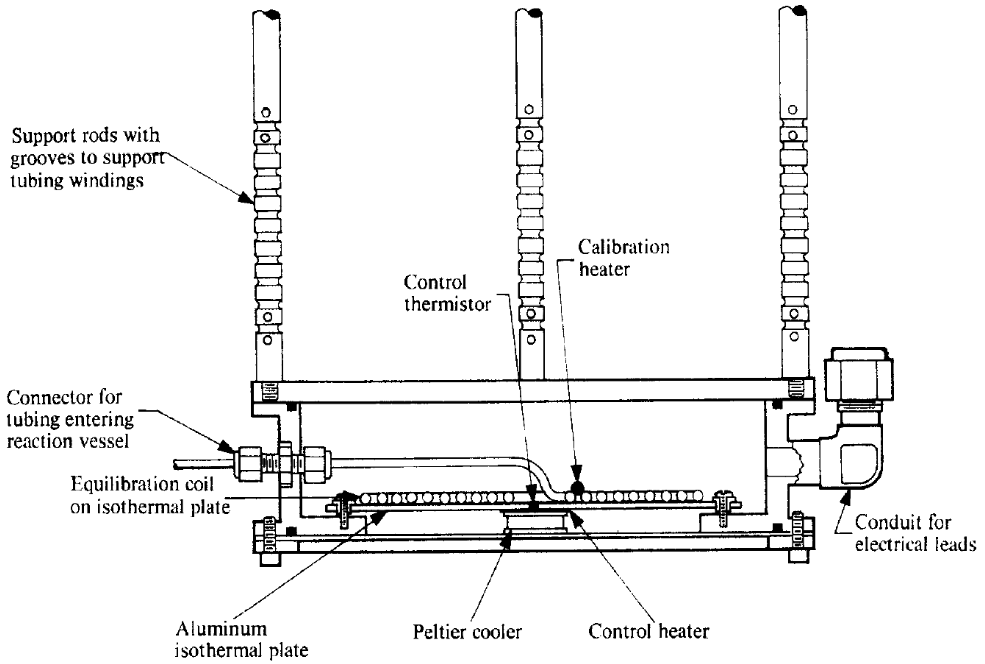
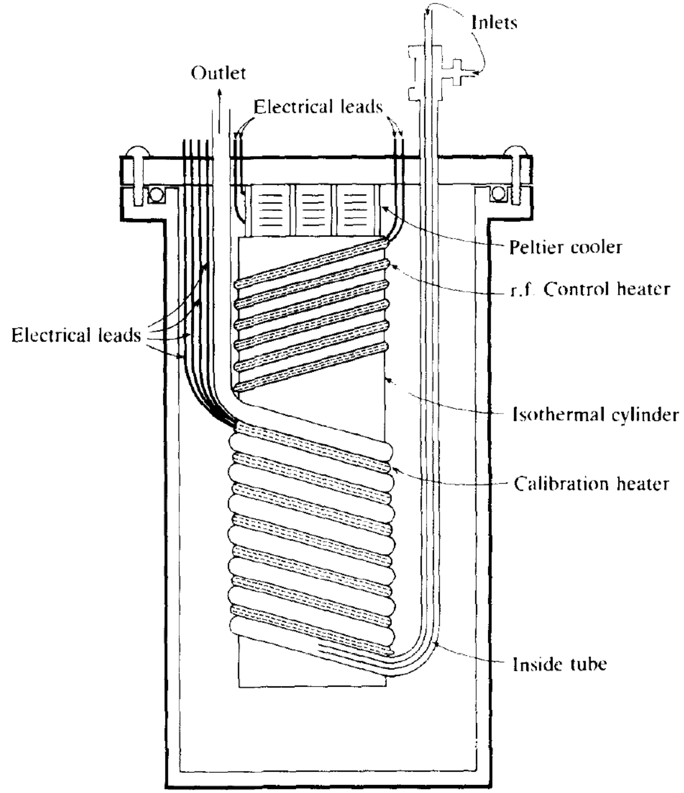


Fig. 1. A schematic diagram of the main components of the calorimeter: 1, pump; 2, pusher; 3, outer can; 4, insulating container; 5, insulation; 6, outer shield; 7, inner shield; 8, reaction vessel; 9, isothermal cylinder; 10, waste solution container; 11, nitrogen tank; 12, pressure gauge; 13, back-pressure regulator; 14, Macintosh Plus computer; 15, computer interface; 16, Tronac PTC-41 temperature controller; 17, Hart Scientific 3704 isothermal control unit.

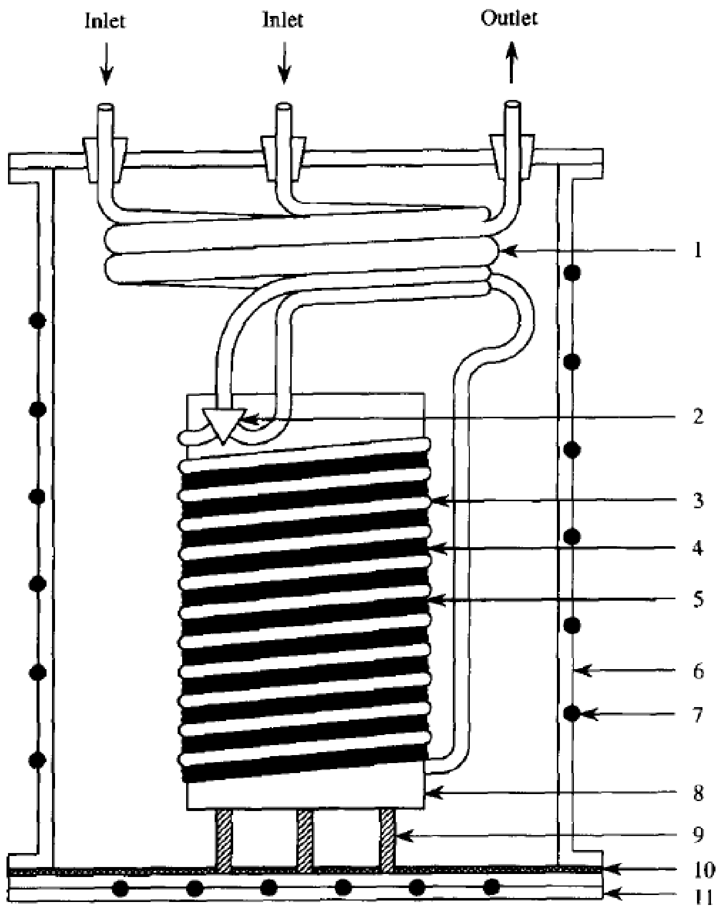
Calorimètre Christensen / Cellule





Compensation de puissance
Mesure : Effets endothermiques - Effets exothermiques
Sensibilité : 3 mW- 2W
Cellules placées dans bain thermostaté

Calorimètre Christensen BYU / Cellules de mélange

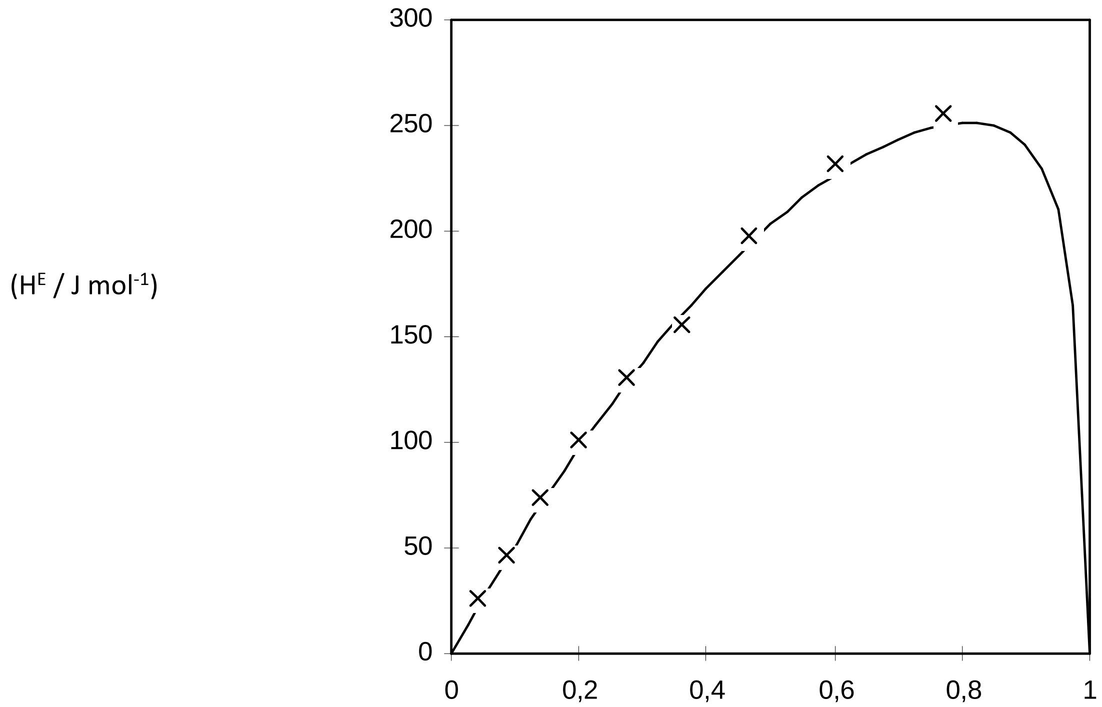


Point de mélange (2)

Tube de mélange (3)
Chauffage (4)
Calibration (5)

Pour les effets exothermiques :
compensation de fuites thermiques

Calorimètre Christensen BYU / Exemple d'Application

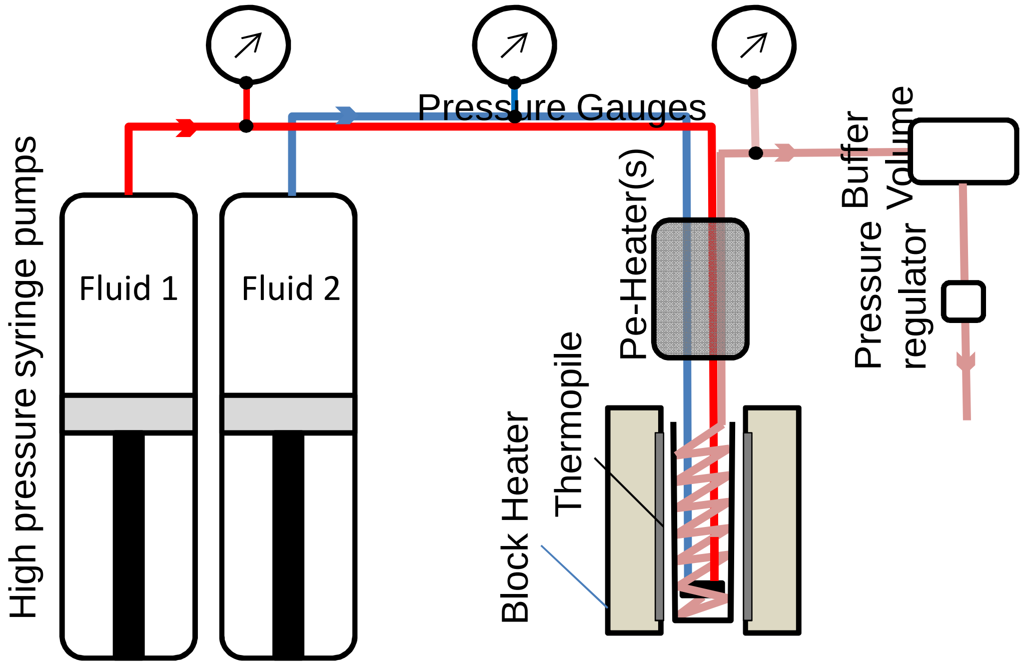


Excess enthalpy of toluene (1) and methanol (2) at –17.8° C and 14.4MPa

× M. Polednicek, V. Majer, V. Hynek, J. JoseReview Of Scientific Instruments 76, 074102 2005

— J.Y. Coxam, S. E. Gillespie, J. L. Oscarson, and R. M. Izatt, J. Chem. Thermodyn. 27, 1133 (1995).

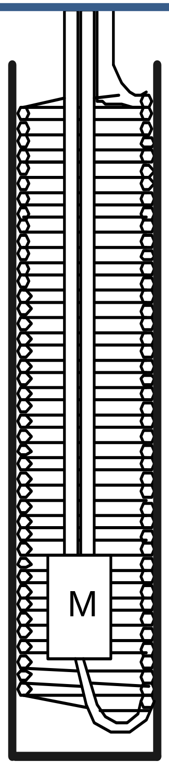
Calorimètre type Calvet / Montage



Calorimètre isotherme à écoulement
T : 173 K - 673 K
P : < 40 MPa
Débit : 0.1 – 1 mL/min

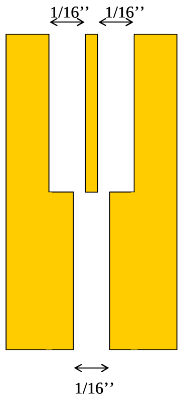
Thermopile
Mesure effet endothermique
effet exothermique
Sensibilité : 0.2 mW- 200 mW

Cellule de mélange



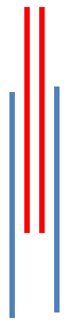
Cellule de mélange
16" o.d. Hastelloy

Point de mélange



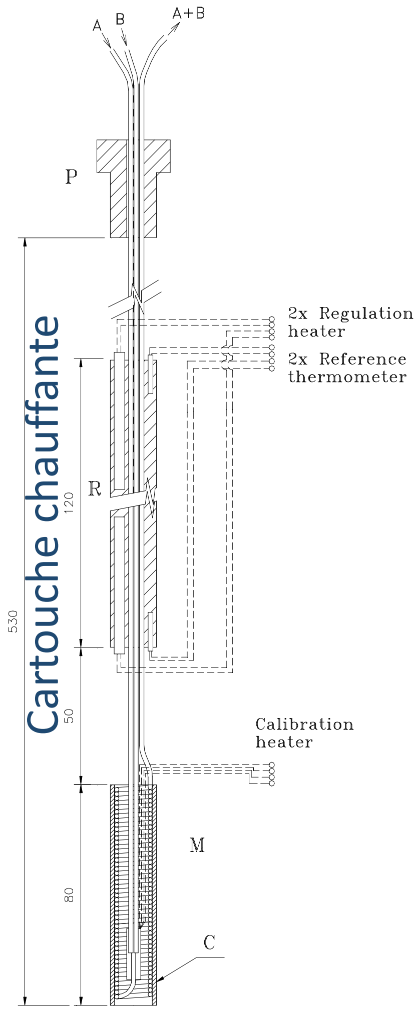
T point

1/32"



1/16"

Tubes concentriques

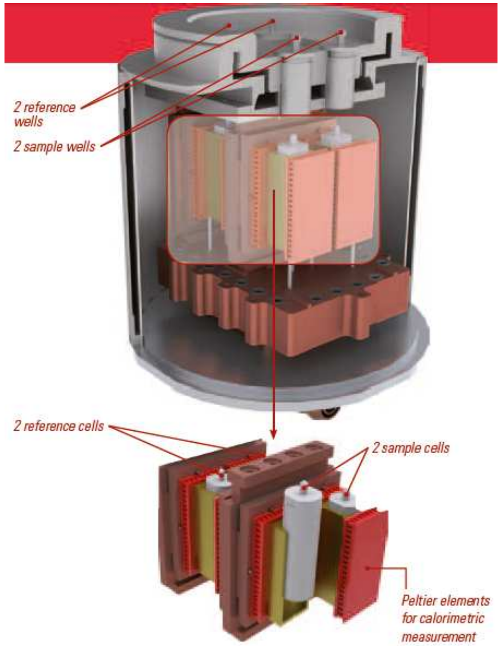


Préchauffage

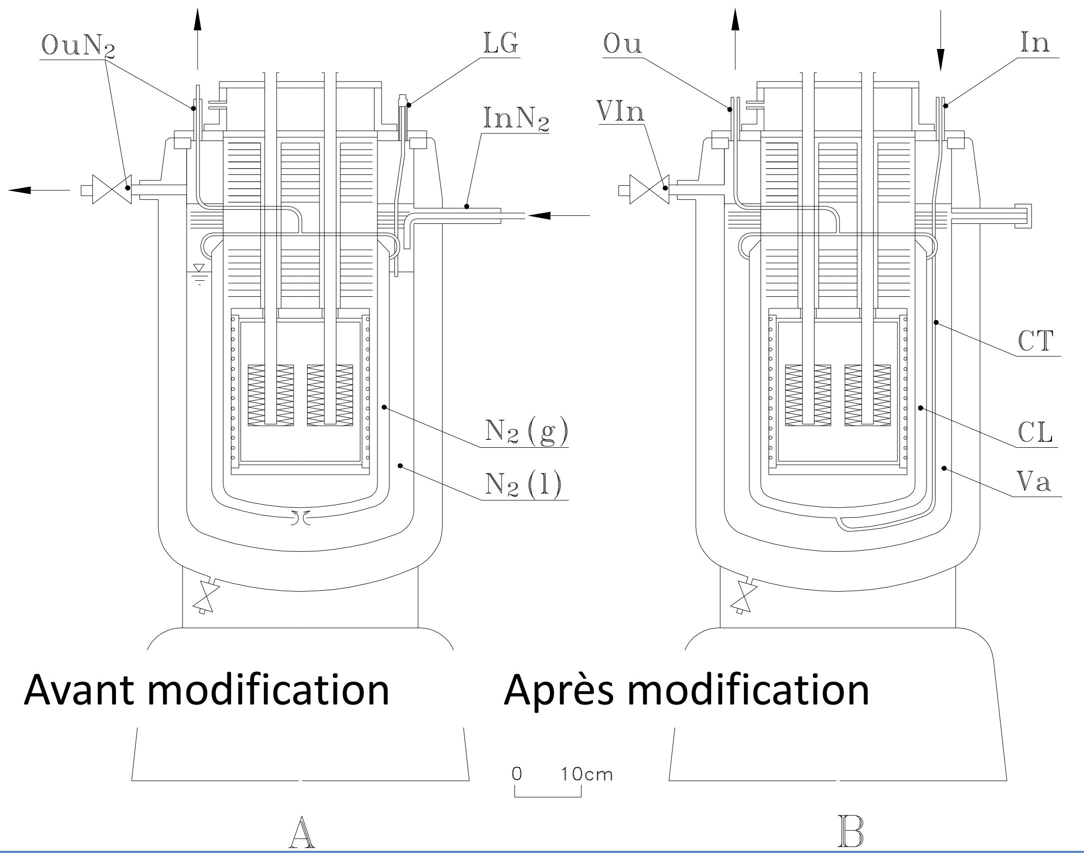
Calorimètre de mélange à basse température

microSC Setaram
-40 to 200°C / cellules Cp ou Cp Hp
Volume : 1mL

SETARAM BT215
Détection flux métrique différentielle
40 µV/mW
signal (20 – 5000 µV)
Température basse : >170 K
Refroidissement : azote liquide



Modification du BT215



Avant modification

Après modification

Modification du BT2.15D

InN_2 : entrée N2 liquide

OuN_2 :sortie N2 gaz;

In : entrée liquide de refroidissement

Ou : sortie liquide refroidissement

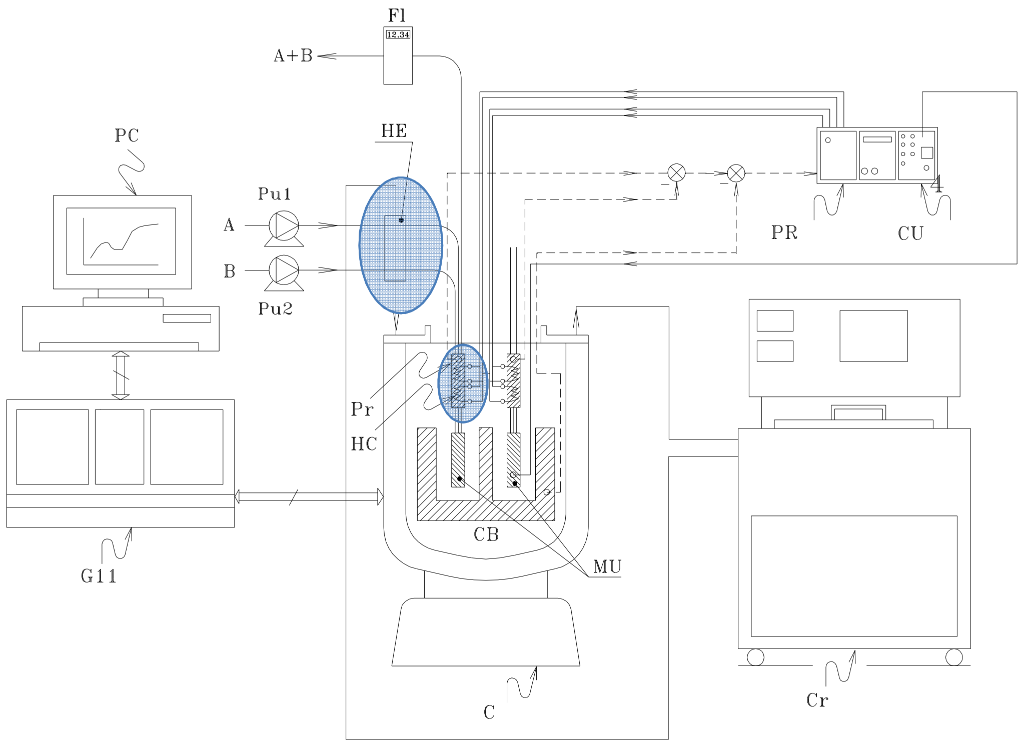
Vin : vide

Va : Zone sous vide

CT-tube de connexion ajouté

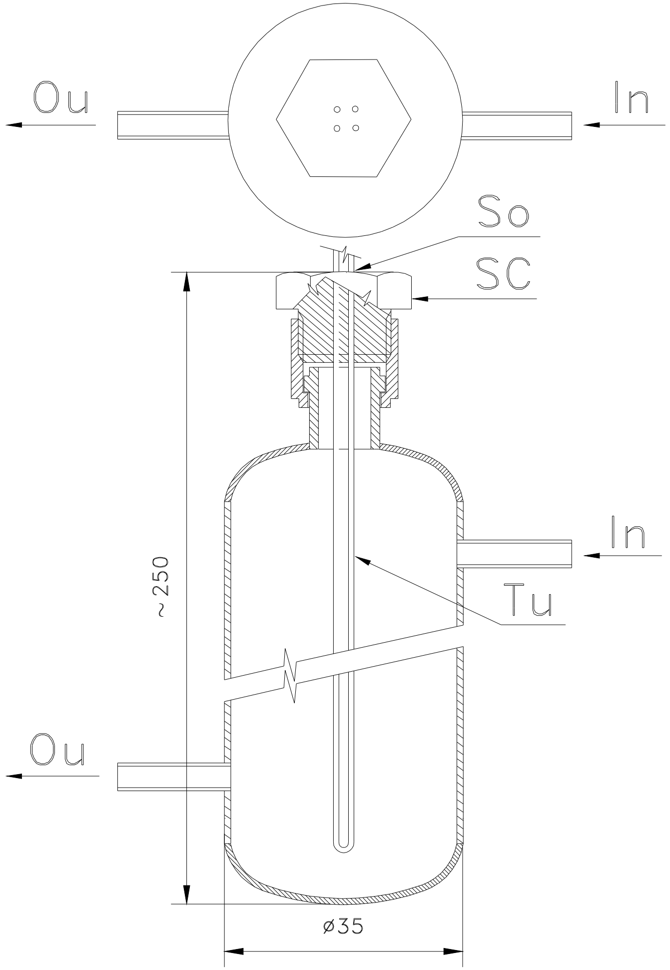
CL- liquide de refroidissement;)

Montage calorimétrique

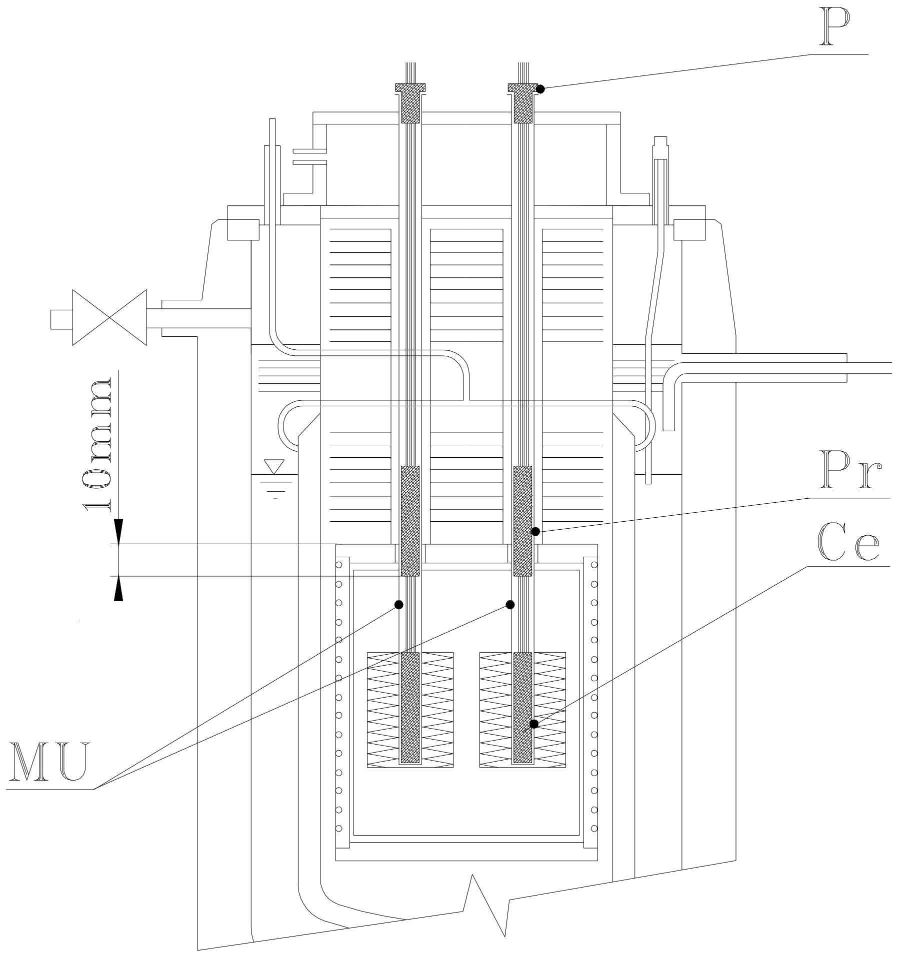


C: calorimétre
Cr: cryostat
HC: cartouche chauffante
HE: échangeur thermique
MU: mixing units;
Pr: pré chauffeur

Mise en température des fluides entrants

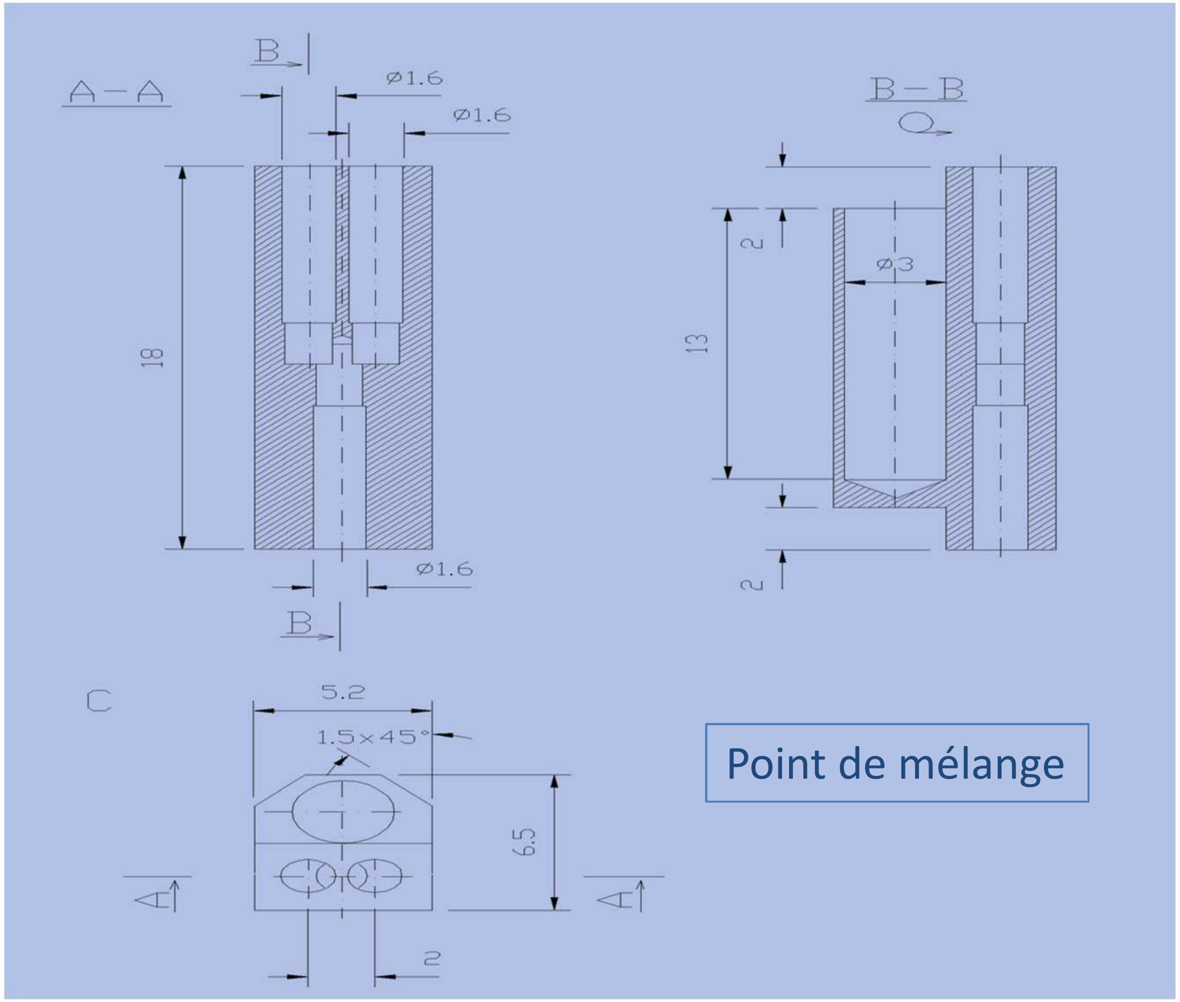


Echangeur thermique



Pré chauffeur

Cellule de mélange



Calibration par effet joule
Resistance chauffante : pt100

Résultats / He □ 1-5 %

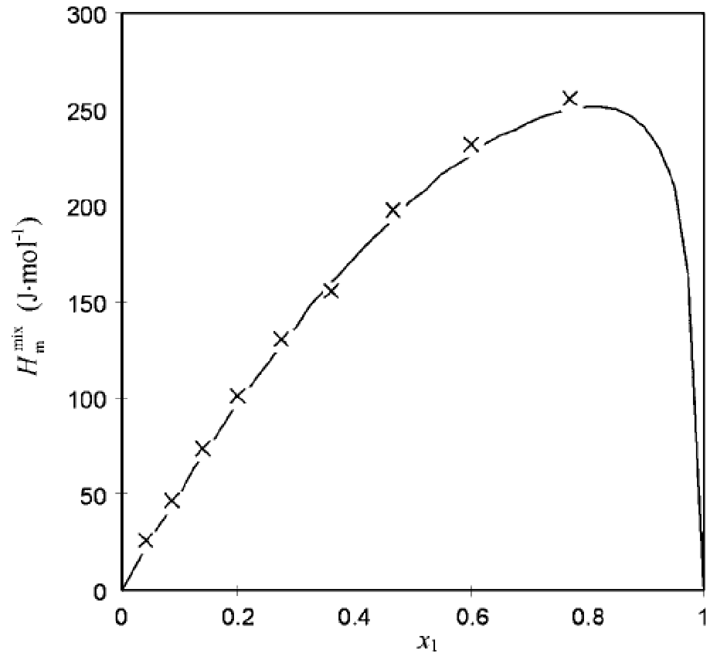
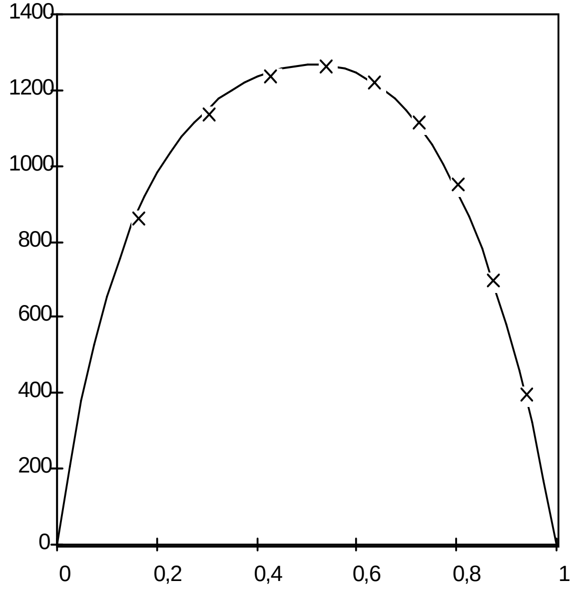


FIG. 9. Heat of mixing of toluene (1) and methanol (2) at −17.8 °C and 14.4 MPa;—Coxam *et al.* (see Ref. 5); × this work.



Excess enthalpy of toluene (1) and methanol (2) at -17.8°C

× Milos Polednicek (2000) Thèse N° 2000CLF22207

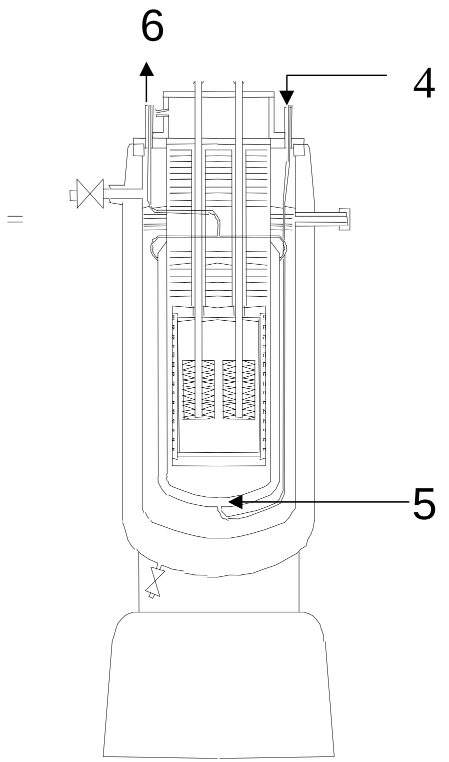
(—) J. Y. Coxam, S. E. Gillespie, J. L. Oscarson, and R. M. Izatt, J. Chem. Thermodyn. 27, 1133- 1995.

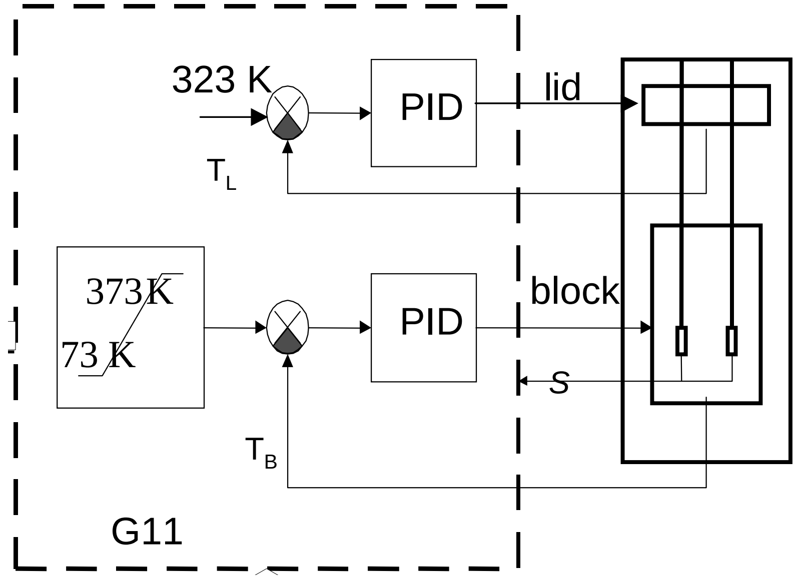
Excess enthalpy of acetone (1) and hexane (2) at -29.95°C;

× Milos Polednicek (2000) Thèse N° 2000CLF22207

(—) K. Schäfer, Int. Data Ser., Sel. Data Mixtures, Ser. A 74-77 (1978).

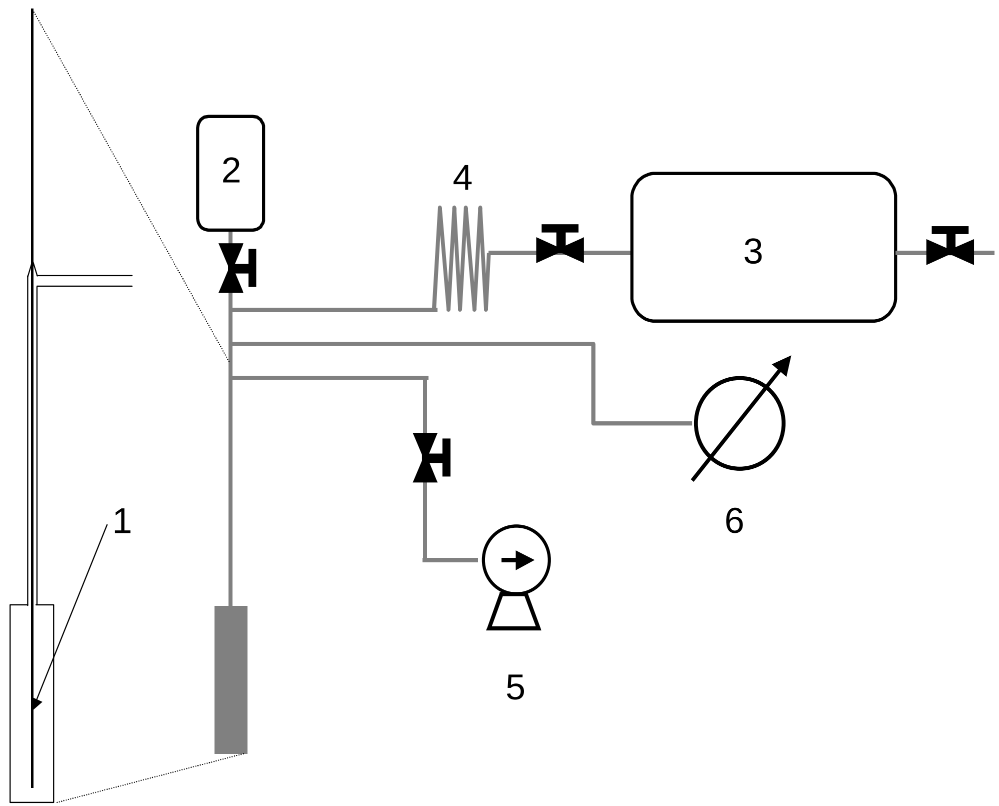
Capacités calorifiques à basse température

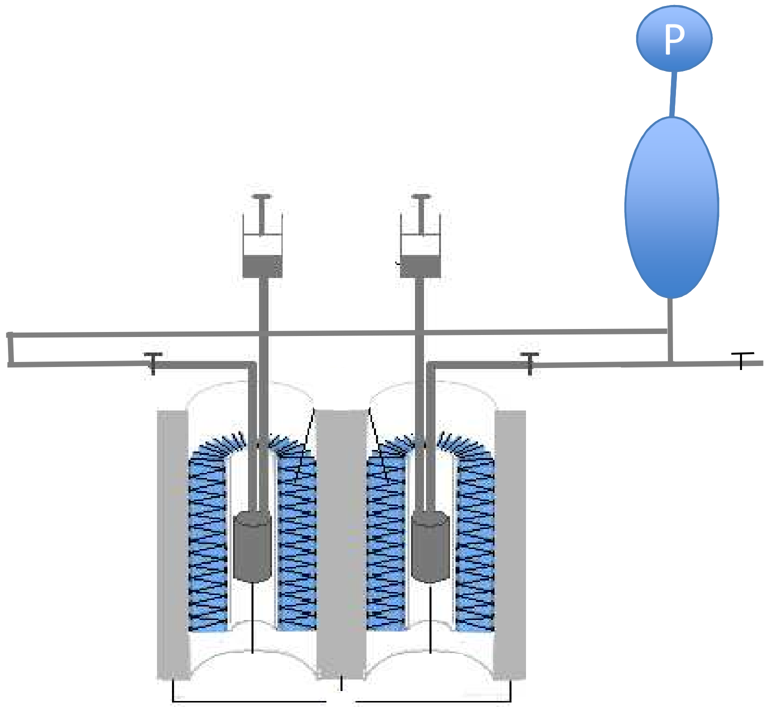




Calorimètre Setaram BT 215 modifié
Cellule : 10 mL
Balayage : 0.05 K/min
p : jusqu'à 30 Mpa
T : 200 K – 300 K

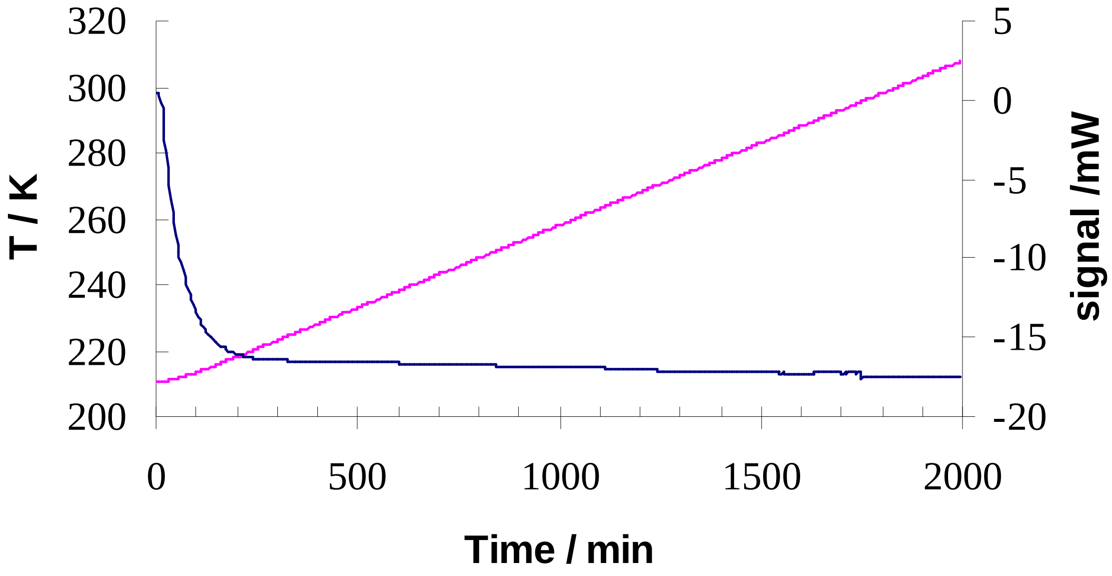
Capacités calorifiques à basse température





1. Tube intérieur de remplissage
2. Cylindre de remplissage
3. Volume tampon pressurisé (gaz inerte)
4. Boucle d'interface échantillon – gaz tampon
5. Pompe à vide
6. Manomètre

Signal calorimétrique en balayage de température



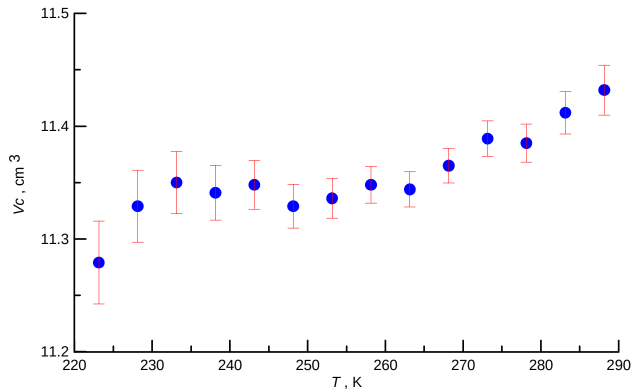
Signal-Temperature versus time curve for an experiment in continuous scanning mode at
0.05 $K.min^{-1}$ (BT)
5 $K.min^{-1}$ (µDSC)

Capacité calorifique

$$\dot{q}_{diff} = \dot{q}_m - \dot{q}_r = \left[\left(m_{f_m} c_{f_m} + m_{c_m} c_{c_m}\right) - \left(m_{f_r} c_{f_r} + m_{c_r} c_{c_r}\right) \right] \frac{\delta T}{\delta t}$$

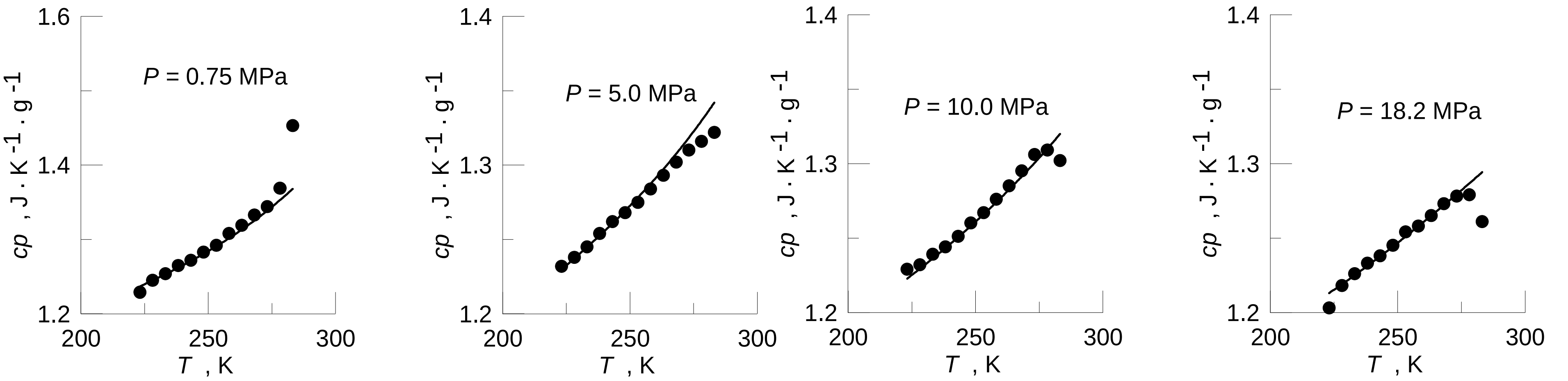
$$c_p = \frac{\left(\dot{q}_{sample} - \dot{q}_{blank}\right)}{m \frac{\delta T}{\delta t}}$$

m: masse de fluide dans la cellule ($m = \rho V$)
V : volume *de la cellule (obtenu par calibration)*



R. Hykrda, J.-Y. Coxam, V. Majer. Int. J. Thermophys., 2004, 25 (6), 1677-1694.

Capacité calorifique (□ 0.5 - 1 %)



Capacité calorifique isobare freon r-134a

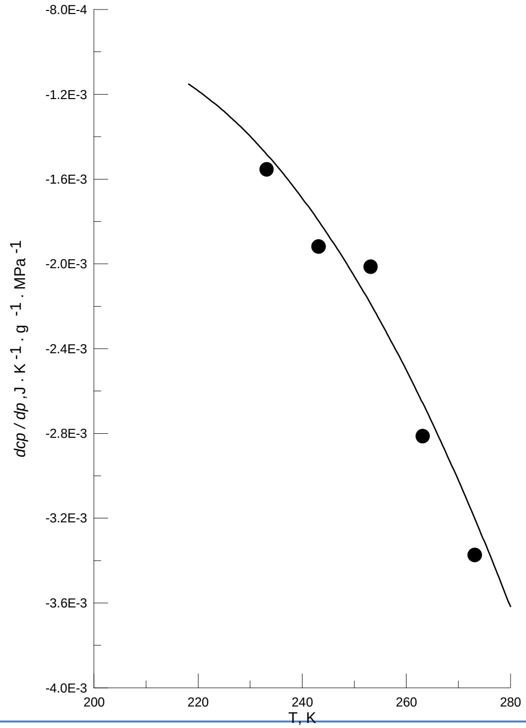
(•) R. Hykrda, J.-Y. Coxam, V. Majer. Int. J. Thermophys., 2004, 25 (6), 1677-1694.

(—) R. Tillner-Roth, H. D. Baehr, *J. Phys. Chem. Ref. Data* **23**: 657 (1994).

Capacité calorifique

Test de cohérence
avec données volumiques

$$\left(\frac{\partial cp}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$$



r-134a at 10 Mpa
(●) Pressure derivative experimental isobaric heat capacities
(-) Second temperature derivative of volume.

Merci